MICROSCOPIC STUDY OF THE SILVER ORES AND THEIR ASSOCIATED MINERALS

A DISSERTATION

SUBMITTED TO THE DEPARTMENT OF GEOLOGY AND MINING AND TO THE COMMITTEE ON GRADUATE STUDY OF THE LELAND STANFORD JUNIOR UNIVERSITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

F. N. GUILD

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OUTLINE.

I. INTRODUCTION.

The increasing amount of space devoted by many of the journals to investigations in which the reflecting microscope is employed, is sufficient evidence of the great value of this new method of attack in the solution of problems of paragenesis of the opaque minerals. That these researches are confined so largely to the investigation of the copper sulphides and associated minerals is the occasion of some surprise. Although in a more or less general way it has been appreciated that the replacements concerned in the process of copper enrichment are common phenomena of nature, yet the fact that these processes may, in their complexity and interest, be duplicated in the deposition of silver minerals, has failed to receive the emphasis it deserved. This is due in part to the greater scarcity of silver minerals and also to the greater difficulty involved in their identification. Moreover, the application of these methods to copper deposits has been a significant factor in the solution of economic problems, and has thus acted as a stimulus for extended researches in those fields. This stage of development has not yet been realized for the silver ores.

The writer became impressed with the attractive features of this unexplored region while investigating certain copper-silver ore specimens from the Silver King mine near Globe, Arizona. It was therefore decided to make a detailed study of the silver ore minerals with the hope that the paragenetic features observed would prove as useful a foundation for further work in this field as has been the epoch-making paper of Graton and Murdoch for copper ores.[1]

The number of minerals which can be determined accurately on polished surfaces by the reflecting microscope alone is exceedingly small. This is particularly appreciated when one undertakes the study of the sulpharsenites and sulphantimonites of lead, copper, and silver. In this connection, however, it should be remembered that the simple tests of determinative mineralogy leave much to be desired in identifying these compounds, espe-

[1] Graton and Murdoch, "The Sulphide Ores of Copper; Some Results of Microscopic Study," *Trans. Am. Inst. Min. Eng.*, Vol. 45, p. 26, 1913.

cially when not well crystallized. At the present time the use of the reflecting microscope in the study of the opaque minerals is confined mainly to the investigation of mineralogical relations rather than identification. While many of the features discussed in the following pages relate to micro-chemical tests and other methods of identification, the main object of the paper is to discuss the principles of ore deposition as revealed on polished specimens. The investigation of many minerals not containing silver will be included since they often play an important rôle in the natural history of the silver minerals.

The order of deposition of the various minerals is found to be surprisingly constant, the later ones replacing the earlier ones in a definite scheme rarely deviated from, so that the minerals may well be described with reference to their position in this scheme rather than by employing the ambiguous terms primary and secondary. With this idea in mind the minerals considered in this investigation will be taken up in the manner already outlined.

II. THE CHARACTERISTIC EARLY MINERALS OF SILVER DEPOSITS. PYRITE, SPHALERITE AND ARSENOPYRITE.

Pyrite.—Pyrite is rarely absent from silver deposits, and according to some authors, plays an important part in the later enrichment of the silver minerals. Thus from geological considerations, Weed[2] has observed that enrichment has not taken place in the absence of this sulphide although the other conditions were favorable. Where pyrite was present abundant rich silver minerals have made their appearance. In the opinion of Cooke[3] these assumptions have been confirmed by his laboratory experiments on the solution of silver minerals in dilute sulphuric acid and the iron sulphates. These are very important considerations. If the presence of ferric sulphate resulting from the oxidation of pyrite is a necessary factor in the deposition of the rich later silver minerals, then downward percolating solutions have accomplished

[2] Weed, "The Enrichment of Gold and Silver Veins," *Trans. Am. Inst. Min. Eng.*, Vol. 30, p. 439, 1900.

[3] Cooke, "The Secondary Enrichment of Silver Ores," *Jour. Geol.*, Vol. 21, p. 1, 1913.

the feat, and these minerals are definitely established as supergene. While there seems to be no doubt that the presence of iron salts in acid solution favors the solution and transportation of many sulphides, it has by no means been proved that they constitute the only solvent for the rich silver minerals. Hypogene solutions are the chief agents in the deposition of vein minerals and that fact alone is sufficient evidence of their great ability as efficient solvents.

Pyrite is normally the first sulphide to form in veins of the common type. It may be preceded by pyrrhotite and arsenopyrite in higher temperature deposits but is followed by sphalerite, tetrahedrite, and galena. In the investigation of the silver ores the appearance of later generations of pyrite has rarely been observed. When so observed it may be found in one of two types: First, as second generation hypogene pyrite, and second, as supergene pyrite (or marcasite). An example of the first case has been noted in a specimen from the Silversmith mine, Sandon, B. C., in which a thin veinlet of pyrite was found crossing sphalerite. In a similar manner it was found crossing tetrahedrite also observed in only one specimen. These occurrences are believed to represent early fractures in which a fresh supply of hypogene solution has entered. The veinlets represent filling rather than active replacement and are therefore evidences of mechanical readjustment rather than a new chemical equilibrium. Supergene pyrite, however, seems to be the result of definite replacement. This has been observed in a specimen of argentite from Freiberg, Saxony, and is illustrated in Plate XVI., *C*. Here the argentite has crystallized in cavities and the replacement by pyrite (or marcasite) has progressed along borders in the form of groups of spheroidal masses with metacolloidal structure. Hintze also notes pyrite as pseudomorph after argentite at Joachimsthal.[4] A similar alteration of polybasite to pyrite (and pyrargyrite) in the Neihart district, Montana, has been observed by Weed.[5] These occurrences call to mind the experiments of

[4] Hintze, "Handbuch der Mineralogie," Bd. I, p. 444.

[5] Weed, "The Enrichment of Gold and Silver Veins," *Trans. Am. Inst. Min. Eng.*, Vol. 30, p. 446, 1900.

Allen who found that iron disulphide as pyrite and marcasite was deposited from a cold solution of low acidity containing ferrous sulphate, sulphur and hydrogen sulphide.[6] Pyrite is thought to have been deposited by descending surface waters in the Georgetown district, Colorado, and is therefore referred to as secondary pyrite.[7]

In silver deposits pyrite is often found to suffer the changes so characteristically observed in the copper veins. Borders and veinlets of chalcopyrite appear which are later replaced by bornite, chalcocite and covellite. The Silver King mine in Arizona, being particularly rich in copper, shows these features to a remarkable degree. Here, as will appear in later descriptions, all the features of copper enrichment are observed parallel with interesting replacements of silver minerals. Stromeyerite plays the same rôle as chalcocite and a complex series of replacements is to be observed, beginning with pyrite and ending with native silver. In deposits where copper is not present in considerable quantities, galena is found to be the most frequent replacing mineral.

Pyrite in association with the silver minerals is shown in Plate X, *A* and *B*. In Fig. *A* pyrite is replaced by chalcopyrite, which is later replaced by galena, while in Fig. B galena replaces pyrite and arsenopyrite directly. The silver minerals have come in later than the galena.

Sphalerite.—Sphalerite is present in the greater number of silver ore specimens studied, a typical example appearing in Plate X., *C*. It is not found actively replacing pyrite, and the evidence of its later age rests upon mechanical relations. Thus it is sometimes observed coming in after a brecciation which has occurred later than the deposition of pyrite. It is commonly filled with minute dots of chalcopyrite arranged in rows and otherwise crystallographically distributed.

The occurrence of later sphalerite has been noted by Blow at Leadville, Colorado, where it is thought to have been dissolved in

[6] Allen, "Sulphides of Iron and their Genesis," *Min. and Sci. Press,* Vol. 103, p. 414, 1911.

[7] Spurr, Garrey and Ball, "Economic Geology of the Georgetown Quadrangle, Colorado," Prof. Paper U. S. Geol. Surv., 63, p. 144, 1908.

the oxidized zone and redeposited below.[8] Emmons, however, is not of the opinion that sphalerite "is precipitated as a secondary mineral along with copper, silver and gold."[9] In all of the specimens studied in connection with this investigation, it is an early hypogene mineral and it has not been observed replacing any of the later sulphides. Minerals found replacing sphalerite are tetrahedrite, galena, chalcopyrite, chalcocite, covellite, stromeyerite and ruby silver.

Arsenopyrite.—Arsenopyrite is probably a high temperature mineral as shown by its presence in pegmatites, contact deposits and magmatic differentiates. It is occasionally present in silver veins where it is found to be still earlier than pyrite ordinarily the first sulphide to be deposited. This is to be expected since its other modes of occurrences show it to be more closely connected with the magmatic period than other vein sulphides. In association with pyrite, galena and proustite it is shown in Plate X., *B,* a photomicrograph of a polished specimen from an unknown locality in Mexico. In this specimen pyrite does not appear to be actively replacing arsenopyrite, but its later deposition is inferred from the fact that the arsenopyrite is greatly fractured while pyrite is still intact. Pyrite was deposited later than the fracturing. The corrosion of arsenopyrite may have furnished arsenic for the proustite molecule.

In a specimen of galena containing arsenopyrite from Rimini, Montana, it appeared in hand specimens as later than galena in the form of tongues and veinlike masses. On examination with the reflecting microscope the veins were found to be crossed and broken up by a network of galena veinlets thus showing its residual character. This peculiarity has also been observed with reference to tetrahedrite. The microscope shows this mineral to be always earlier than galena, yet in hand specimens forms are observed that might lead to the reverse conclusion.

[8] Blow, "Geology and Ore Deposits of Iron Hill, Leadville, Colo.," *Trans. Am. Inst. Min. Eng.*, Vol. 18, p. 171, 1889–1890.

[9] Emmons, "The Enrichment of Sulphide Ores," Bul. 529, U. S. Geol. Surv., p. 143, 1913.

III. THE EARLY SILVER MINERALS.

Argentiferous Galena and Tetrahedrite.

Galena.—Galena with a varying percentage of silver is one of the most common minerals in silver deposits in which it occurs replacing the earlier sulphides including arsenopyrite, pyrite, sphalerite, tetrahedrite and chalcopyrite. In Plate X., *B*, it is seen replacing both pyrite and arsenopyrite. In Plate X., *D*, it is seen to replace tetrahedrite and chalcopyrite. Pyrite and arsenopyrite are not replaced by it in case the later minerals mentioned above are also present. This fixes its position in the order of deposition quite definitely as follows: (1) Arsenopyrite, (2) pyrite, (3) sphalerite, (4) tetrahedrite, (5) chalcopyrite, (6) galena. The rich silver minerals are still later as will appear in the descriptions to follow. The comparatively late appearance of galena might lead one to place it among the supergene minerals. Rarely, however, does it seem to be associated genetically with oxidation processes in such a way as to suggest deposition from descending solutions. Blow found veinlets of galena penetrating limestone directly below the oxidized ores.[10] Irving and Bancroft state positively that a portion of the galena at Lake City, Colo., is connected with oxidation processes.[11] The great insolubility of galena under surface conditions has been well pointed out by Emmons. Its occurrence in outcrops, in placers, and the fact that it has frequently been plowed up in the fields of the Wisconsin zinc district are convincing evidences of this property.[12]

Since galena is considered to be the source of much of the silver appearing in deposits of the precious metals, it is a matter of great interest to determine if possible the form in which the silver exists. There are at least three possibilities. First, the silver molecule usually thought to be argentite may be present as a solid solution or isomorphous constituent; second, it may occur as in-

[10] Blow, "Geology and Ore Deposits of Iron Hill, Leadville, Colo.," *Trans. Am. Inst. Min. Eng.*, Vol. 18, p. 169, 1889–1890.

[11] Irving and Bancroft, "Geology and Ore Deposits near Lake City, Colo.," Bul. U. S. Geol. Surv., No. 478, p. 97, 1911.

[12] Emmons, "The Enrichment of Sulphide Ores," Bul. U. S. Geol. Surv., No. 529, p. 138, 1913.

clusions or microscopic particles of definite minerals; and, third, it may occur in the form of submicroscopic particles. Nissen and Hoyt have conducted laboratory experiments with the hope of throwing some light on the subject.[13] They found that lead sulphide when fused was capable of absorbing or holding in solid solution on cooling less than 0.2 per cent. silver sulphide. The excess separated out in the form of definite grains of argentite as shown by their photomicrographs. These experiments were not performed under the same conditions of temperature as existed in the veins when the deposition of galena took place and therefore are not conclusive. It is quite possible that very different relationships between the two sulphides may exist at the lower temperature of deposition from water solution. Nevertheless field observations have strongly suggested conclusions similar to those arrived at by Nissen and Hoyt. Thus in the silver deposits of Bingham, Utah, Boutwell found those ores to assay highest in silver which contained the largest amount of some other silver mineral, in this case tetrahedrite (freibergite). Ranking next to these were the "black sulphides" thought to contain tellurides and last of all the pure galena samples.[14] In the silver deposits near Lake City, Colo., Irving and Bancroft report that "little of the argentiferous galena is rich in silver in any of these districts unless accompanied by tetrahedrite or some rich secondary silver mineral." Surfaces were polished and when no admixtures were observed the assay values indicated only 10 to 15 ounces per ton.[15]

A large number of specimens of argentiferous galena from various localities was investigated by a comparative study of polished surfaces and quantitative determinations and many instructive features observed. On etching the surface with nitric acid or hydrogen peroxide, all galena grains showing above 0.10 per cent. silver revealed an appreciable number of spots of either argentite or tetrahedrite, frequently both. These spots were fre-

[13] Nissen and Hoyt, "Silver in Argentiferous Galena Ores," Econ. Geol., Vol. 10, p. 172, 1915.

[14] Boutwell, "Economic Geology of the Bingham Mining District," Prof. Paper, U. S. Geol. Surv., No. 38, p. 113, 1905.

[15] Irving and Bancroft, "Geology and Ore Deposits near Lake City, Colo.," Bul. No. 478, U. S. Geol. Surv., p. 56, 1911.

quently so minute that even when present in great abundance, the percentage of silver was not raised above 0.39 per cent. Such a specimen from Rimini, Mont., is illustrated in Plate XI., *A*. In this specimen the microscopic inclusions are of four distinct minerals, three of which could be identified. Tetrahedrite appeared harder than galena and could be recognized by its relief. Moreover it could be compared with other grains in the specimen of sufficient size to permit of micro-chemical tests. Argentite appeared slightly softer than galena and was practically invisible before etching. Ruby silver could also be distinguished by its bluish tint as compared with galena. The fourth mineral, also softer than galena, may have been polybasite, stephanite or some of the sulfo-salts of lead or copper. Only when the spots appeared to be of considerable size, in fact visible with a hand lens, did the percentage reach 0.50. These begin to show evidence of a later addition of the silver mineral with the exception of those containing tetrahedrite. This mineral then has the characteristic appearance of residual grains left over in the replacement of tetrahedrite by galena. The grains become more numerous or larger as tetrahedrite areas of considerable size are approached. The later entrance of the rich silver minerals is illustrated in Plate XI., *B*, representing a polished specimen from Tonopah, Nev., and Plate XI., *C*, a specimen from the Reco mine, Sandon, B. C. In Plate XI., *B*, the spots are proustite and are associated with thin veinlets of the same mineral not shown in the photograph. Identical structures have been observed in specimens of galena from Freiberg, Saxony, which contained 1.12 per cent. silver. Plate XI., *C*, shows pyrargyrite following cleavage directions in galena. The specimen, as assayed by the methods described below, contained 0.54 per cent. silver.

On the other hand, specimens of argentiferous galena showing on etching only occasionally spots of the silver minerals were found to contain less than 0.10 per cent. silver. Thus galena from the Bunker Hill mine, Cœur d'Alene district, Idaho, showing only now and then in the field of view one spot contained 0.08 per cent. silver. Another specimen from the same mine sometimes with three spots in the field of view contained 0.09 per cent. silver.

A specimen from the Hercules mine showing an occasional spot gave 0.108 per cent. silver. Areas in the same hand specimen with 25 to 30 spots in the field of view (No. 5, Leitz objective) contained 0.24 per cent. silver. These spots were practically all identified as tetrahedrite. A specimen of galena was found in the Old Yuma mine, Pima Co., Arizona, showing no spots over large areas. This contained only 0.016 per cent. silver.

These results show that silver may exist in galena to *nearly* 0.10 per cent. in the form of submicroscopic particles or solid solutions. Isomorphous mixtures with the silver minerals are certainly not formed. Above the limit mentioned, spots of silver minerals begin to appear in constantly increasing numbers as the percentage of silver rises.

The method of procedure in making the determinations described above consisted in selecting from the polished surfaces as pure areas as possible, etching with nitric acid, and after examining with the reflecting microscope, breaking up with a sharp awl sufficient of the material for scorification and cupellation. From 100 to 500 milligrams were found sufficient except in case of the very lean specimens when one gram was taken where possible. The spots were found to be grouped very unevenly so care had to be exercised in not cutting too deeply thus decreasing the possibility of the sample representing different conditions from those recorded on the surface.

Tetrahedrite.—Tetrahedrite when argentiferous (freibergite) becomes an important mineral of silver. Analyses show as high as 36.90 per cent. silver.[16] This is present as an isomorphous mixture of some silver molecule. While frequently important economically, it is doubly interesting from the standpoint of paragenesis. Microscopic investigation shows it to be a more prolific source of the later silver minerals than is galena. Indeed, much of the galena in the silver deposits has replaced tetrahedrite and its silver content is thus due to residual spots of silver-bearing tetrahedrite as well as argentite from the breakdown of the complex molecule.

Tetrahedrite has frequently been mentioned in geological de-

[16] Hintze, "Handbuch der Mineralogie," Bd. I., p. 1118.

scriptions as an early mineral. In the Cripple Creek district it persists to a depth of 2,000 feet below the surface.[17] It is an early mineral at Butte, Montana, although the corresponding arsenic compound, tennantite, is thought to be later.[18] It is described as secondary, on the other hand, at Bingham, Utah,[19] and Rio Tinto, Spain.[20] It is still more emphatically described as a late mineral in the Georgetown Quadrangle, Colorado. It is stated to be "the last of the silver minerals to form."[21] The writer has invariably found tetrahedrite earlier than the rich silver minerals and even earlier than galena, as illustrated in Plate X., *D*. Its most common relation to sphalerite is shown in Plate X., *C*, a photomicrograph of material from the Silver King mine in Arizona. Occasionally it is found actively replacing sphalerite as appears in Plate XI., *D*, from a specimen of the Silversmith mine, Sandon, B. C. Residual masses of sphalerite are frequently found so that tetrahedrite may definiteley be placed later than sphalerite.

As suggested above tetrahedrite easily gives way to attacking solutions, and it may thus form the starting point for a series of reactions by which minerals richer than itself in silver are developed even finally ending up with native silver. Thus in Plate XII., *A*, also from the Silver King mine, it is found with a complex system of veinlets of stromeyerite which in places enlarge to areas of considerable size. This type of alteration has been observed in many specimens, another example being given in XII., *B*, from an unknown locality in Colorado. The alteration has set in around quartz grains and along cracks. The further breakdown of stromeyerite will be described later. In the breakdown of the tetrahedrite molecule illustrated in Plate XII., *A*

[17] Lindgren and Ransome, "Geology and Ore Deposits of the Cripple Creek District," Prof. Paper, U. S. Geol. Surv., No. 54, p. 121, 1906.

[18] Weed, Emmons and Tower, U. S. Geol. Surv., Butte Special Folio, No. 38, p. 6, 1897

[19] Boutwell, "Economic Geology of the Bingham Mining District," Prof. Paper, U. S. Geol. Surv., No. 38, pp. 107, 220, 1905.

[20] Finlayson, "The Pyrite Deposits of Huelva, Spain," ECON. GEOL., Vol. 5, p. 411.

[21] Spurr, Garrey and Ball, "Economic Geology of the Georgetown Quadrangle, Colo.," Prof. Paper U. S. Geol. Surv., No. 63, p. 261, 1908.

and *B*, the sulphide of antimony has been removed leaving the sulphides of copper and silver, some of which appear as the double salt $Cu_2S \cdot Ag_2S$. If the silver-copper portion of the tetrahedrite molecule be taken as $3R_2S, Sb_2S_3$,[22] and the ratio of silver to copper be considered as 2 : 1, a possible reaction is suggested in the equation below:

$$(Cu_2S)_2, Ag_2S, Sb_2S_3 = Ag_2S \cdot Cu_2S + Cu_2S + Sb_2S_3.$$

Later it will be shown that much of the stromeyerite is mingled with an excess of the chalcocite molecule so the presence of the extra copper sulphide in the above reaction is accounted for. What becomes of the antimony sulphide cannot be definitely stated, though it seems probable that it enters into the formation of complex silver molecules as ruby silver, polybasite or stephanite. These minerals are often found associated with tetrahedrite and are even found replacing it in veinlets.

Tetrahedrite as observed on polished surfaces varies considerably in hardness and color, a condition which causes some confusion in identification. This is due to its great variability in composition. As shown by tables of analyses in Dana's "System of Mineralogy," copper varies from 10.8 per cent. to 44.08 per cent.; silver from a trace to 31.29 per cent.; zinc from nothing to 7.25 per cent.; and iron from 0.64 per cent. to 8.24 per cent. Polytelite is thought to belong here, being a lead-zinc variety with less than 1 per cent. copper. Micro-chemical tests on small fragments secured from polished surfaces show that much of the silver-bearing variety is low in copper. In addition to the causes in variability mentioned above the mineral grades into tennantite, the arsenical variety of fahlerz. Although it varies in hardness from 3 to 4, all varieties show more relief than the silver minerals, a very important feature in identification.

Separate determinations of silver have been made on tetrahedrite and galena grains in specimens of typical rich silver ores, from 50 to 100 milligrams of the material being secured from the

[22] Prior and Spencer, "Chemical Composition of Fahlerz," *Min. Mag.*, Vol. 12, p. 193. These authors propose the formula,

$$3R'_2S, Sb_2(As_2)S_3 + x(6R''_2S, Sb_2(As_2)S_3).$$

polished surfaces by means of a sharp awl. The tetrahedrite even under high power was seen to be perfectly homogeneous showing the silver to be isomorphously mixed, while the galena as usual showed spots. In a specimen from the Nettie L. mine, Ferguson, B. C., tetrahedrite grains were found to contain 7.27 per cent. silver while the galena contained 0.23 per cent. A similar specimen from the Silver King mine, Arizona, showed 6.06 per cent. silver for the tetrahedrite grains, while the galena contained 1.24 per cent. These grains of galena, however, contained spots of tetrahedrite that could be seen by a hand lens. Still another specimen of tetrahedrite from the Reco mine, Sandon, B. C., showing on polished surfaces many spots and veinlets of ruby silver (proustite), contained 25.02 per cent. silver. These grains had, of course, been enriched by late additions.

IV. THE LATE SILVER MINERALS.

Stromeyerite, $Cu_2S \cdot Ag_2S$.—Stromeyerite is one of the rarer ore minerals of silver and but little reference regarding its characteristics or paragenesis is found in published descriptions in which the reflecting microscope is employed. Murdoch describes it as having a purplish tint when viewed side by side with chalcocite and to have sometimes a smooth and sometimes a ragged surface. He also reports that it is etched by nitric acid and develops cleavage in some grains.[23]

In the silver ores thus far studied stromeyerite has been found to present two types of occurrences. First, in veinlets and areas of considerable size associated with tetrahedrite (freibergite) and doubtless derived from it. This type has already been described under tetrahedrite and is illustrated in Plate XII., *A* and *B*. Second, as a replacement product of bornite. In this type it seems to play the same rôle as chalcocite in copper ores. There are scattered residual grains of pyrite almost completely replaced by chalcopyrite, which in its turn has altered to bornite, later to be replaced by stromeyerite and chalcocite. All of these transformations with the exception of the first is illustrated in Plate

[23] Murdoch, "The Microscopic Determination of the Opaque Minerals," p. 117, 1916.

XII., *C*, a photomicrograph of a polished specimen from the Silver King mine, Arizona. Pyrite, although present in the specimen, does not appear in the photograph. An incipient replacement of bornite in a specimen from the same locality is illustrated in Plate XII., *D*. This presents the appearance of a crude graphic structure. Replacements less often observed are galena by stromeyerite, when it takes place along borders, and chalcopyrite by stromeyerite. An interesting case of the latter replacement was observed in a specimen from Mt. Lyell, Tasmania, and is illustrated in Plate XIII., *A*. The replacement has progressed in such a manner as to give rise to the so-called graphic intergrowth so frequently described. A similar "intergrowth" between chalcocite and bornite has been described from this locality by Gilbert and Pogue.[24] These authors held that the structure indicated contemporaneous deposition of the two sulphides. These structures are beautifully developed in several varieties of the silver minerals and will be discussed more fully later.

The polished surfaces of stromeyerite in many of the specimens studied show a peculiar complicated structure which has been the subject of considerable investigation to determine its origin. It occurs most frequently as an intricate mass of blades somewhat resembling oleander leaves in shape, arranged in great confusion or roughly grouped in designs. The blades have a perceptible purplish tint and are slightly softer than the groundmass. The structure is best brought out by polishing on the felt wheel so as to develop considerable relief. By the use of a red screen to darken the purplish tint, the structure may be brought out fairly well for photographic purposes as shown in Plate XII., *C*. On etching with potassium cyanide solution, however, the design is brought out in a striking manner as appears in Plate XIII., *B*. The harder and lighter tinted material constituting the background of the design is more severely acted upon by the reagent and appears nearly black. The blades are only slightly affected, so that by rubbing lightly on cloth they become quite free from the black coating that first appears. The structure as shown in Plate XIII.,

[24] Gilbert and Pogue, "Mt. Lyell Copper District," *Proc. Nat. Mus.*, Vol. 45, p. 609.

B, is often very uniformly developed throughout a considerable area, although occasionally both the purplish blades and the whiter groundmass enlarge to patchy masses. This is illustrated in Plate XIII., *C* and *D,* photomicrographs from a specimen from an unknown locality in Arizona. Each area is smooth, the transition sometimes being through the bladed structure while at others more abrupt. On etching with potassium cyanide solution the soft smooth areas are only slightly acted upon while the faintly harder portion marked "*cc*" is blackened and cleavage lines are developed (Plate XIII., *C*). The transition borders etch exactly as is found to be the case in many of the other specimens of stromeyerite (Plate XIII., *B*). The explanation of this structure is that the design is caused by a mixture of stromeyerite and chalcocite, the former constituting the purplish blades which are thus set in a background of chalcocite. This opinion is practically substantiated by both qualitative and quantitative tests. The purplish surface marked "*st*" reacts strongly for silver in addition to copper, while the area marked "*cc*" (XIII., *C*), reacts for silver but slightly. Two specimens of stromeyerite have been found which do not show the complicated structure, one being from Tombstone, Arizona, and the other from Mt. Lyell, Tasmania. The material from Tombstone was not adapted for quantitative determinations, as it was found under high power to be filled with minute specks of native silver, probably a breakdown product of the silver mineral. Fairly pure material could be secured from the polished surface of the Tasmania specimen, which yielded, after scorification and cupellation, 44.40 per cent. silver. The amount of material worked upon was only 13.8 milligrams. It still contained a few admixed particles of chalcopyrite which could not be removed. Material secured in the same manner from surfaces showing the complicated structure contained only 23.48 per cent. silver, which corresponds to 44.2 per cent. of the double molecule, Ag_2S, Cu_2S, the remainder doubtless being chalcocite. The low percentage of silver in the material showing a homogeneous surface (theory requires 53.05 per cent.) may be due to the chalcopyrite or some chalcocite in solid solution. These results together with the

microscopic evidence are considered conclusive ground for regarding the complicated structure observed in some specimens of stromeyerite to be due to a complex mixture of the chalcocite molecule and stromeyerite.

The two components making up the stromeyerite structure having been identified, it now remains to discuss the causes which have developed the interesting feature. In this matter little more can be done than to suggest the possibilities. First, it may represent the unmixing of a solid solution, or breakdown of an isomorphous mixture. According to this theory the two sulphides Ag_2S and Cu_2S were, under the conditions of formation, first deposited as an isomorphous mixture or solid solution. Later as conditions changed the material found itself unstable and broke up into the two molecules $Cu_2S \cdot Ag_2S$ and Cu_2S. The results of microscopic examinations show that under present conditions silver sulphide and copper sulphide do not remain mixed in all proportions. In other words stromeyerite appears to be a definite double salt. Transition between it and chalcocite is not characterized by a fading off of one into the other but by the complex mingling of distinct individuals (Plate XIII., *C* and *D*). Further, published chemical analyses seem to show the ratio of copper sulphide to silver sulphide to remain rather persistently near the ratio 1 : 1. Thus in the table of analyses given by Hintze, eight out of seventeen correspond very closely to the ratio given. Seven have an excess of copper and two an excess of silver.[25] Were the mineral an isomorphous mixture there would certainly have been greater variation. Jalpaite, a mineral of the formula $3Ag_2S$, Cu_2S, and isometric in crystallization, has been described from Jalpa, Mexico, and Tres Puntas, Chile.[26] Margottet obtained in the laboratory isometric crystals corresponding to the formulæ $2Ag_2S$, Cu_2S and $3Ag_2S$, Cu_2S, the latter having the composition of jalpaite.[27] These facts suggest the possibility of various combinations taking place under proper conditions other than

[25] Hintze, "Handbuch der Mineralogie," Bd. 1, p. 542.

[26] *Ibid.*, Bd. 1, p. 458.

[27] Quoted by Hintze, "Handbuch der Mineralogie," Bd. 1, p. 542.

that expressed by the ratio 1 : 1. These on breaking down might develop a complicated structure.

Second, the structure may be caused by replacement, a theory strongly suggested in Plate XIII., *C* and *D*. Then the complex borders are replacement phenomena resulting from the attack of silver solutions upon chalcocite or copper solutions upon stromeyerite. The occurrence of stromeyerite around the borders of chalcocite areas, as is sometimes observed, also favors this theory.

Third, the structure may have resulted from the segregation or recrystallization of metacolloidal material. According to this theory the sulphides of silver and copper resulting from the breakdown of freibergite or other minerals are at first mingled in a colloidal condition which on becoming crystalline develop the peculiar structure described. This is the theory rather favored by the writer, though it is thought that any one of the three processes may have been active in individual cases. Then the structure simply represents a final state of equilibrium reached whenever these materials are brought together by whatever causes. Even if the first mentioned theory be the correct one, segregation would have to take place before the constituents of the breakdown could develop the present structure.

A beautiful so-called intergrowth between stromeyerite and galena of quite a different design has been observed in specimens from the Silver King mine, Arizona (Plate XIV., *A*). and from Cobalt, Ontario. In appearance it is much like the eutectic structure of alloys. It is very fine and requires an oil-immersion lens to bring out the structure satisfactorily. In only one specimen had the white areas developed sufficiently to show the characteristic triangular pits of galena. The small areas showing the pseudo-eutectic structure are sometimes angular, as though originally a definite crystal, while at others the borders are extremely irregular.

In the attempt to explain the origin of this structure the same three possibilities mentioned above might be considered. Since it is a deposition from solution it cannot in any way be looked upon as a true eutectic.

Graphic intergrowths have frequently been described in the

journals, and until recently have been held by most authors to be due to simultaneous deposition of the two sulphides. This has been in accordance with Laney's hypothesis advanced in 1911.[28] Rogers in 1914 suggested that the structure was due to replacement[29] and in 1916 described material from several new localities and showed conclusively that in the cases cited by him, his explanation was correct.[30] Whitehead had also arrived at the same conclusion.[31] The intergrowths of galena and stromeyerite here described are much more intricate than those thus far explained and the evidence that they are due to replacement is not at all conclusive. No transition types have been observed by which a clue to the origin of the structure could be ascertained. The writer is inclined to think that it is due to a readjustment of subcrystalline or colloidal mixture which may have resulted from a breakdown of solid solution or been an original precipitate from aqueous solution.

Stromeyerite with an excess of the argentite molecule apparently develops a structure that can hardly be distinguished from the stromeyerite-galena intergrowth. This has been observed in a specimen from Mt. Lyell, Tasmania.

Pyrargyrite, $3Ag_2S, Sb_2S_3$ and Proustite, $3Ag_2S, As_2S_3$.—The ruby silvers rank among the most important silver minerals in many of the rich deposits of the United States and elsewhere. Invariably these minerals are thought to have been deposited late in the history of ore deposition. Thus Spurr describes pyrargyrite as coating crevices that cut the primary ore.[32] It is also found in the oxidized material and is thought to have been deposited by descending solutions. In the same district argentite, polybasite and stephanite are thought in part to be "primary"

[28] Laney, "The Relation of Bornite and Chalcocite in the Copper Ores of the Virgilina District of North Carolina and Virginia," Econ. Geol., Vol. 6, p. 399, 1911.

[29] Rogers, *Min. and Scientific Press*, Vol. 108, p. 609, 1914.

[30] Rogers, "The So-called Graphic Intergrowth of Bornite and Chalcocite," Econ. Geol., Vol. 11, p. 582, 1916.

[31] Whitehead, "The Paragenesis of Certain Sulphide Intergrowths," Econ. Geol., Vol. 11, p. 1, 1916.

[32] Spurr, "Geology of the Tonopah Mining District," U. S. Geol. Surv. Prof. Paper, No. 42, 1905.

minerals. Irving and Bancroft find it associated with the latest deposited minerals of the vein and restricted to the upper levels of the mine.[33] Ransome holds that the ruby silver minerals together with stephanite and polybasite are as characteristic of downward enrichment as chalcocite.[34] As already pointed out the early minerals of silver are confined mainly if not entirely to tetrahedrite and argentiferous galena. They are therefore held to be the source of the later enriched products. Tetrahedrite is probably the most prolific source as shown by microscopic investigations, and the fact that the late silver minerals are most often arsenic or antimony compounds. Thus the results obtained from the study of polished surfaces are in accord with the earlier geological observations, at least, in respect to the late deposition of these minerals. They are observed replacing sphalerite, tetrahedrite and galena.

Proustite replacing galena which in its turn has replaced pyrite and arsenopyrite is illustrated in X., *B,* a photomicrograph of a polished specimen from an unknown locality in Mexico. Its occurrence as spots in argentiferous galena (Plate XI., *B*) has already been described. A veinlet of pyrargyrite in galena is shown in Plate XI., *C*. Proustite and galena occurring as veinlets in sphalerite is illustrated in Plate XIV., *B,* the specimen being from Schemnitz, Hungary. Stephanite is found in other portions of the same section (*A*) and exhibits similar features. Photographs might be added illustrating how the ruby silvers replace tetrahedrite in the same manner. It is occasionally observed breaking down into native silver (Plate XIV., *C*, Durango, Mexico). In a specimen of argentite from Freiberg, Saxony, it appears replacing the silver sulphide in spots and borders around impurities.

In a specimen from Tonopah, Nev., pyrargyrite and proustite are associated with each other in an interesting manner as illustrated in Plate XIV., *D,* and Plate XV., *A*. These are evidently

[33] Irving and Bancroft, "Geology of the Ore Deposits near Lake City, Colo.," Bul. U. S. Geol. Surv., No. 478, p. 63, 1911.

[34] Ransome, "Criteria of Downward Sulphide Enrichment," Econ. Geol., Vol. 5, p. 211, 1910.

cavity fillings, as shown by drusy quartz borders, frequently with sharp euhedral crystals. Empty cavities are also present in the specimen, and the arrangement of the quartz grains, as shown in thin section, also favors this explanation. In Plate XIV., *D*, pyrargyrite occupies the central portion, the borders being proustite, the earlier of the two to be deposited. Proustite appears faintly bluer than pyrargyrite in reflected light, yet when freshly polished the contrast is so slight as to be just barely perceptible. It would have been impossible to represent this occurrence photographically were it not for the peculiar differential action of the electric arc. The central portion, pyrargyrite, is rapidly tarnished by the unprotected arc, bright effects being first produced along the border, continued action causing a blacking of the whole surface. When the arc is of low intensity or protected by ground glass or the daylight screen employed for visual work, little or no tarnishing effect is observed. The blackened surface was examined under an oil-immersion lens, when a perceptible rectangular design could be made out. This feature has been observed in other silver minerals, notably in some samples of argentite. The blackening develops at times with such rapidity as to make photographing difficult. In Plate XV., *A*, the arrangement is reversed, proustite occupying the center with an incomplete border of pyrargyrite. In the lower portion of the photograph tetrahedrite, the mineral showing relief, appears as a thin rim between the two. This enlarges and forms the whole of the border in the upper portion. It is thought that the cavity was first filled with tetrahedrite which was later nearly replaced by proustite, leaving a narrow border. Later pyrargyrite came in, replacing tetrahedrite along the margin of the projecting quartz crystals, still leaving a residual rim of tetrahedrite. In the upper portion of the photograph, pyrargyrite failed to appear. If this explanation is correct, the order of deposition of the two ruby silvers is the same in each case and they are both later than tetrahedrite as usual.

These minerals were identified by micro-chemical tests, as well as by simple microscopic tests of small fragments broken up from the polished surface by a sharp point. Proustite is light red in thin fragments, while pyrargyrite is deep cherry red on the thin

borders, approaching opacity in the thick centers. The streaks are also very characteristic, proustite being cherry red and pyrargyrite dark purplish red or brown. This test may also be made by crushing small fragments on glazed paper. Tetrahedrite reacts for copper and shows higher relief than any of the silver minerals.

Other cavity fillings similar to those described above, in which the two ruby silvers were mingled in a very intricate manner, were observed in specimens from the same locality. A striking feature was the sharp boundary between the two minerals, a grading off of one into the other never having been observed. This is in accordance with the investigations of Miers, who from crystallographic and chemical considerations, concluded that proustite and pyrargyrite formed distinct species and are not perfectly isomorphous.[35]

In a specimen containing the ruby silvers from Schemnitz, Hungary, proustite was found in beautiful so-called intergrowth with galena (Plate XV., *B*). The small area showing the pseudo-eutectic structure was completely enclosed by pyrargyrite, which on exposure to the electric arc became darkened, as appears in the illustration. The elongated area showing the unusual structure seems to be a residual mass remaining after replacement by pyrargyrite. The galena portions project slightly into the pyrargyrite, showing an inequality in the ease of replacement. The origin of structures of this kind where transitionary stages have not been found is still in doubt.

Plate XV., *C*, was taken from a veinlet consisting of an intricate mixture of pyrargyrite and proustite in calcite from the Cobalt district of Canada. Marcasite has developed in fine divergent forms resembling organic growths. It is believed that the iron disulphide has developed later than the silver minerals, a very rare occurrence for this substance as discussed more fully under pyrite. At Goldfield, Nev., however, it frequently appears later than the other sulphides of the district.[36]

[35] Miers, "Contribution to the Study of Pyrargyrite and Proustite," *Min. Mag.*, Vol. 8, p. 57.

[36] Ransome, "The Geology and Ore Deposits of Goldfield, Nev.," Prof. Paper, U. S. Geol. Surv., No. 66, p. 115, 1909.

Stephanite, $5Ag_2S, Sb_2S_3$.—Stephanite is one of the less common minerals of silver and often when found in association with other sulphides is in such small particles as not to permit a satisfactory study of its paragenesis. It is a late mineral and in general is found in occurrences similar to the ruby silvers and other sulpho-salt minerals. The factors which have caused this mineral to develop rather than pyrargyrite have not yet been worked out. It may be due merely to the relative concentration of silver and antimony in the vein solutions. Stephanite with kernels of pyrargyrite have been described from Freiberg, Germany,[37] and many other cases are on record where it is found in intimate association with the sulpho-salt minerals of silver. It seems to show rather a strong tendency to replace gangue material. Thus Fenner has described an interesting occurrence of this mineral from Colorado, in which the constituents of rhyolite porphyry have been replaced by stephanite and chalcopyrite. In one section described chalcopyrite replaced the groundmass, while stephanite appeared later replacing feldspar phenocrysts.[38] Bastin has mentioned stephanite as a rare constituent associated with polybasite, proustite, galena, etc., in the later minerals of the silver veins of Gilpin Co., Colo.[39]

Stephanite replacing fragments in brecciated material was observed in a specimen from the Reco mine, Sandon, B. C., and is illustrated in *D*. The brecciated material consisted of quartz with calcite cement and formed an interesting mosaic with pyrite, sphalerite, galena and stephanite. The ore minerals were too disseminated in this specimen to permit a determination of the order of deposition. In another section from the same locality (Plate X., *A*) it is seen in close association with other sulphides. Pyrite is fractured and replaced to small degree by chalcopyrite in the form of borders and veinlets. Sphalerite is later than pyrite and is replaced by galena. Stephanite is then deposited after which a later generation of chalcopyrite crosses both galena

[37] Hintze, "Handbuch der Mineralogie," Bd. I., p. 1155.

[38] Fenner, "A Replacement of Rhyolite Porphyry by Stephanite and Chalcopyrite at Leadville," *Sc. Mines Quar.*, Vol. 31, p. 235, 1909–10.

[39] Bastin, "Metasomatism in Downward Sulphide Enrichment," Econ. Geol., Vol. 8, p. 51, 1913.

and stephanite. The order of deposition then is: (1) Pyrite, (2) sphalerite, (3) chalcopyrite, (4) galena, (5) stephanite, and (6) late chalcopyrite. Still another specimen showing sphalerite, galena and stephanite, also from the same district, is illustrated in Plate XVI., *A*.

Stephanite may be identified on polished surfaces by its inferior hardness, gray color, duller than galena, black fragments absolutely opaque when examined under a high-power microscope with transmitted light, micro-chemical reaction for silver and failure to respond to the test for copper (tetrahedrite and polybasite).

Polybasite, $9Ag_2S\,(Cu_2S)\,Sb_2S_3$.—Polybasite does not show any paragenetic features that differentiate it from the other antimony or arsenic compounds of silver. It is later than galena and appears cutting the still older sulphides, sphalerite, and tetrahedrite. At Tonopah, Nev., according to Spurr, it is found as deep as 500 feet below the surface and may be deposited by ascending solutions.[40] It is described by Bastin as a secondary mineral replacing galena.[41] The corresponding arsenic mineral, pearceite, has been observed by Whitehead, in specimens from the Gemini mine, Tintic, Utah, in graphic intergrowth with galena.[42] It is believed to be replacing galena. In the Little Belt mountains, Mont., it has been described as "an alteration product of galena, and to be mixed with and to grade into pyrargyrite, which in some cases is its undoubted alteration product."[43]

Several occurrences similar to those described above have been studied by the writer. Thus it is illustrated, associated with galena in a veinlet crossing sphalerite, in Plate XVI., *B*, a photomicrograph of a polished specimen from Guanacevi, Mexico. Here it has replaced galena, which has earlier replaced sphalerite.

[40] Spurr, "Geology of the Tonopah Mining District," Prof. Paper, U. S. Geol. Surv., No. 42, p. 95, 1905.

[41] Bastin, "Metasomatism in Downward Sulphide Enrichment," Econ. Geol., Vol. 8, p. 51, 1913.

[42] Whitehead, "Paragenesis of Certain Sulphide Intergrowths," Econ. Geol., Vol. 11, p. 1, 1916.

[43] Weed and Pirsson, "Geology of the Little Belt Mountains, Mont.," 20th Ann. Rept. U. S. Geol. Surv., Pt. 3, p. 411, 1899.

In a specimen from the Seven Thirty mine near Georgetown, Colo., tetrahedrite appeared as residual grains surrounded by polybasite in which were found numerous wavy streaks of proustite. The two silver minerals were doubtless alteration products of arsenical tetrahedrite.

Polybasite as viewed on polished surfaces is considerably duller than galena and may easily be distinguished from tetrahedrite, which it closely resembles in color, by its inferior relief. It is distinguished from stephanite and pyrargyrite by the presence of copper, which is always in isomorphous mixture with the silver. It is sometimes cherry red on the thinnest edges like pyrargyrite.

Argentite, Ag_2S.—From the numerous descriptions of the occurrence of argentite, it would seem that it may be either a hypogene or supergene mineral. Thus great masses were found in the upper zones of the Comstock lode. Such bonanzas usually directly underlie the oxidized material and the evidence seems to be conclusive that they were deposited by supergene solutions. Yet in the Comstock lode, for example, argentite has been identified at a depth of 3,000 feet below the surface.[44] At Tonopah, Nev., also some occurrences are held to be primary while others are thought to be secondary.[45] Many other examples might be cited showing that there is abundant evidence in support of both the hypogene and supergene origin of this mineral. In both of these cases, however, it was a late mineral to be deposited, probably just later than galena and earlier than second generation chalcopyrite.

Emmons has expressed surprise that argentite is not more often found metasomatically replacing other sulphides, a reaction which he believes should take place on account of its position as the lowest member in the solubility scale.[46] In the specimens studied during this investigation, argentite is rarely found to have actively replaced the earlier sulphides. It is most often found in small

[44] Emmons, "The Enrichment of Sulphide Ores," Bul. U. S. Geol. Surv., No. 529, p. 120, 1913.

[45] Spurr, "Geology of the Tonopah Mining District, Nevada." U. S. Geol. Surv. Prof. Paper, No. 42, p. 22, 1905.

[46] Emmons, *loc. cit.*, p. 121.

particles filling cavities in gangue material, and associated with galena, and the late silver minerals as pyrargyrite, proustite, etc. On the other hand, argentite seems to yield easily to the attack of vein solutions. Almost every specimen shows the breakdown into native silver to greater or less degree. This may occur as borders reaching out more or less into the cracks of adjacent minerals, as delicate wandering veinlets, or it may be recrystallized in large crude masses. One specimen from Butte, Montana, showed thousands of minute specks of silver evenly sprinkled throughout the mass, all of such minute size that they were invisible except under high power. These occurrences will be more fully described in the section on native silver.

Replacement of argentite by a late generation of pyrite has already been mentioned. This observation was made on a specimen from Freiberg, Saxony, and is illustrated in Plate XVI., *C*. A late generation of chalcopyrite has frequently been observed replacing the rich silver minerals. Argentite was found to be no exception. Thus in Plate XVI., *D*, we have an illustration of cavity filling by argentite, from Butte, Mont., where the borders have become delicately replaced by a fringe of chalcopyrite probably supergene. The argentite has purposely been darkened by the action of the electric arc, in order to show contrast between the argentite and chalcopyrite. The same specimen shows minute dots and dashes of ruby silver, which is probably a late replacement product.

Argentite replacing smaltite in a complex system of veinlets has been observed in specimens from Cobalt, Ont., and is illustrated in Plate XVII., *A*. Patches of stromeyerite occur in the argentite areas. Both are replaced here and there by native silver and less often by a late generation of chalcopyrite. The latter mineral is frequently observed to grade off into light yellow areas which on examination with high power are found to consist of an exceedingly fine "intergrowth" of chalcopyrite and argentite (or stromeyerite). The two constituents were arranged in angular outline too intricate to admit of reproduction. This is believed to be a replacement phenomenon, since the grading off occurs on borders of chalcopyrite masses.

An intergrowth of argentite and stromeyerite identical in appearance with that of stromeyerite and galena (Plate XIV., *A*), except that the argentite areas appeared duller than the corresponding galena, has been observed in material from Mt. Lyell, Tasmania. This, as explained before, is thought to represent some sort of equilibrium in areas where there is more of the argentite molecule than is necessary to form stromeyerite.

Native Silver.—Native silver is believed to have ordinarily been formed by the alteration of the earlier silver minerals, mainly argentite. It has also frequently been described as coating the ruby silvers, polybasite, etc. It is said to be "primary" in the zeolitic copper ores of Lake Superior.[47] It sometimes persists to great depths as in the Aspen mining district of Colorado, where it is found crossing barite 900 feet below the surface.[48] At Creede, Colorado, it is found 1,200 feet below the surface.[49] It has generally been assumed that silver is typically a supergene mineral, yet the compounds of silver are known to be weak and should therefore easily break down under a variety of conditions. As early as 1843 Bischof found that superheated steam was capable of reducing argentite to metallic silver, which appeared in arborescent shapes very much as in nature. Other minerals of silver treated in the same way yielded similar results.[50] These experiments have been repeated from time to time and modified, Moesta even finding that the reaction could take place at 100 degrees.[51] From considerations of this kind, coupled with geological data, Katō thinks that native silver in certain ore deposits of Japan was deposited by hypogene solutions.[52] From Vogt's

[47] Emmons, "The Enrichment of Sulphide Ores," Bul. U. S. Geol. Surv., No. 529, p. 118, 1913.

[48] Lindgren, quoted from oral communication in Emmons, "The Enrichment of Sulphide Ores," Bul. U. S. Geol. Surv., No. 529, p. 118, 1913.

[49] Emmons, *loc. cit.*, p. 119.

[50] Bischof, "Einige Bemerkungen über die Bildung der Gangmasses," *Pogg. Ann.*, 60, p. 285.

[51] Quoted by Vogt in his paper: "Ueber die Bildung des gediegenen Silbers, besonders des Kongsberger Silbers, durch Secondärprocesse aus Silberglanz und anderen Silbererzen," *Zeit. prakt. Geol.*, Vol. 7, p. 113, 1899.

[52] T. Katō, "The Ore Dejosits in the Environs of Hanano-Yama, near the town of Ōda, province of Nagato, Japan," *Meiji College of Technology Journ.*, Vol. 1, No. 1, p. 32.

article on native silver at Konsberg one might well arrive at a similar conclusion concerning the paragenesis of some of the silver at that locality. He states that "die Reduction des Silberglanzes zu metallischen Silber geschah hauptsächlich schon früher als die Bildung des Kalkesphates und des Flussspathes, des Magnetkies und des jüngeren Schwefelkies, also ungefähr gleich nach der Auskrystallization des Silberglanzes."

In the investigation of the silver minerals cases have been observed where the complex silver minerals have broken down into native silver. The occurrence of native silver in the form of thousands of microscopic specks in a specimen of stromeyerite from Tombstone, Arizona, as well as a similar occurrence in argentite from Butte, Montana, has already been mentioned. This is the first step in the breakdown of the earlier silver mineral, solution, transportation and recrystallization being necessary for the production of the delicate structure so frequently observed. In Plate XVII., *B*, is seen illustrated a veinlet of silver in an argentite specimen from Butte, Mont. The same specimen showed rough masses of native silver around the borders of the argentite areas. A somewhat similar veinlet is seen in XII., *C*, filling a crack in stromeyerite and associated minerals, and expanding into a mass of considerable size. Plate XVII., *C*, shows the characteristic manner in which stromeyerite breaks down into native silver as observed in the specimens from the Silver King mine, near Globe, Arizona. The silver is arranged in beautiful filiform structure, the branches of which envelop individual chalcocite grains, some of the finer filaments even extending into fracture and cleavage cracks of the chalcocite, thus completing the intricate design. Occasionally areas are found where the whole design is roughly oriented with reference to cleavage directions of chalcocite. All of these features are well brought out by etching with potassium cyanide solution, when the outline of the individual grains, as well as their cleavage, is made clearer. The areas showing the structure described grade into stromeyerite, when the native silver disappears altogether, or is confined to borders, veinlets or clumps of more or less rounded outline (Plate XII., *C*). The causes which have been responsible for the

filiform structure now become clear. Stromeyerite has broken down into chalcocite and native silver. The chalcocite has crystallized into definite grains of varying size. The silver in recrystallizing has formed around these grains, extending everywhere into the minutest cracks. As would naturally be expected, the silver is also found crystallizing in cracks and along borders of other minerals both gangue and ore. Palmer and Bastin have shown that many metallic ores, among them chalcocite, precipitate in the laboratory free silver from a silver sulphate solution.[53] This action may, in a measure, contribute to the development of the filiform structure, a molecule of chalcocite always being at hand to precipitate silver should a soluble salt be formed from the argentite portion of the double molecule.

Native silver resulting from the breakdown of ruby silver has already been mentioned and is illustrated in Plate XIV., *C* (Durango, Mexico). Plate XVII., *D* shows spots of native silver in a veinlet of tetrahedrite crossing smaltite from the Cobalt district, Ontario. In other specimens from the same locality containing more massive tetrahedrite (freibergite), numerous bunches of mossy silver were observed with their spaces filled with an intimate mixture of pyrargyrite and proustite. Here the tetrahedrite had first broken down into the ruby silvers, which still later yielded native silver.

Other specimens have been examined, in which the mineral associated with the native silver and apparently, at least, replaced by it, has not been its source. In such cases the associated mineral may have been a precipitant for silver-bearing solutions, or it may have been itself earlier replaced by a silver mineral, which later broke down completely into the native metal. Characteristic examples of the first case are to be observed in specimens of cobalt-silver ores from the Cobalt district, Canada, illustrated in Plate XVIII., *A* and *B*. Here veinlets of native silver are seen replacing smaltite and niccolite. In Plate XVIII., *A*, the large silver vein is found to have followed up a niccolite vein, which had earlier formed by replacement of smaltite. In other portions of

[53] Palmer and Bastin, "Metallic Minerals as Precipitants of Silver and Gold," Econ. Geol., Vol. 8, p. 140, 1913.

the same specimen silver is found in veinlets crossing niccolite areas. This association calls to mind the researches of Palmer, who found niccolite to be an especially good precipitant of silver in silver sulphate solutions.[54] Plate XVIII., *B*, presents some features which have not yet been satisfactorily explained. These are, first, the presence of euhedral crystals of smaltite set in a groundmass of native silver, and second, the presence of a central mass of silver (or sometimes bismuth, as illustrated in Plate XX., *B*), surrounded by a more or less concentric arrangement of the cobalt and nickel minerals. Plate XVIII., *B*, is of too high a magnification to show this relation to the best advantage. It is better illustrated for bismuth in Plate XX., *B*. The silver and bismuth are without doubt later than the associated minerals, as illustrated by vein relations, yet they are characteristically found in the centers of spherical or botryoidal masses. This structure will again be referred to in the discussion of the associated cobalt and nickel minerals.

Plate XVIII., *C* and *D*, show the replacement of bornite by native silver possibly via stromeyerite. The specimen in which these structures were observed was also from the Cobalt district. Plate XVIII., *D*, resembles some of the so-called graphic intergrowth and, as shown by transitional types, is a replacement phenomenon. Other specimens from Cobalt show stromeyerite replacing bornite. This calls to mind a somewhat similar feature observed in material from the Silver King mine, Arizona, in which stromeyerite has replaced bornite in a rough graphic design (Plate XII., *D*). A further replacement of stromeyerite by silver would develop a structure similar to that shown in Plate XVIII., *A*.

Plate XIX., *A* and *B*, illustrate a peculiar dendritic structure of smaltite and silver in calcite from Cobalt, Ontario. In Plate XIX., *B*, it will be seen that the smaltite has the same shell-like form enclosing native silver as is so frequently in these ores. An examination of the borders between smaltite and silver seems to indicate that a replacement of smaltite by silver has taken place. The dendritic structure then becomes a phenomenon of smaltite, silver solutions having later replaced the cores of the regularly

[54] Palmer, "Studies in Silver Enrichment," Econ. Geol., Vol. 9, p. 664, 1914.

arranged smaltite grains. Shells of smaltite enclosing gangue are illustrated in Plate XX., *D*. While these shells do not show dendritic grouping, a replacement of the gangue in the centers would develop a structure similar to that seen in individual grains or shells illustrated in Plate XIX., *B*.

Cerargyrite.—Although native silver is the natural end product in the transformation of the various silver minerals, it may itself be the object of attack of supergene solutions containing chlorids or hydrogen sulphide. Its alteration to cerargyrite has been observed in specimens from the Stonewall Jackson mine, near Prescott, Arizona, and is illustrated in Plate XIX., *C*. The gangue is siderite and the silver occurs embedded in it in rough grains showing all grades of alteration to the chloride. Argentite is also present in small grains and may have been the source of the free silver.

Vogt has observed the breakdown of argentite into native silver, which in its turn has formed argentite again partly by the action of hydrogen sulphide formed from decaying mine timbers and blasting powder.[55]

Huntilite, Ag_3As? and Dyscrasite, Ag_3Sb to Ag_6Sb.—Only one specimen of so-called huntilite from the original locality, Silver Islet, Lake Superior, was examined. It consisted of fine dendritic replacements in dolomite, which under the reflecting microscope were found to be made up of a central portion of a cream mineral like dycrasite, surrounded by rims of native arsenic. The occurrence is illustrated in Plate XIX., *D*. The central portion (huntilite ?) became slightly darkened on etching with nitric acid thus giving sufficient contrast to make the photograph possible.

One specimen of dyscrasite from the Cobalt district, Ont., was studied. Under high power it showed in places a faint complicated structure perhaps due to unmixing of a solid solution. This was brought out more strikingly on etching with nitric acid which yielded rather definite grains of etched material closely crowded

[55] Vogt, "Ueber die Bildung des gediegenen Silbers, besonders des Kongsberger Silbers, durch Secondärprocesse aus Silberglanz und anderen Silbererzen," *Zeit. prakt. Geol.*, Vol. 7, p. 113, 1899.

together and set in a background of less affected material. The mass was associated with smaltite into which extended small veinlets of dyscrasite.

Brongniardite, PbS, Ag_2S, Sb_2S_3.—This mineral was discovered by Damour in 1849.[56] Only massive material has been found, the isometric crystals described by Damour in 1854[57] having been proved by Prior and Spencer to be the entirely different species, stanniferous argyrodite.[58] Murdoch finds some specimens to appear to be a mixture of ruby silver, galena(?), and possibly miargyrite. Others show a distinct mineral close to argentiferous jamesonite.[59]

One specimen of brongniardite from Chococomete, Bolivia, was examined by means of the reflecting microscope. It was found to show a structure almost identical in appearance to the blue and white effect in some chalcocite. The pattern appeared in some places in patchy designs, in others in parallel bands calling to mind the polysynthetic twinning of the feldspars. In places there were two series of bands crossing at an angle. The bluish streaks were found to be pyrargyrite as suggested by Murdoch. When examined in fragments this portion was shown to be transparent on thin edges and to have a deep cherry red color. These streaks were also found to be rapidly darkened when exposed to the unscreened electric arc. This, as mentioned before, is a peculiar effect produced on certain of the silver minerals notably pyrargyrite and argentite. A polished surface of brongniardite etched in this manner is illustrated in Plate XX., *A*. The pyrargyrite streaks show a darkening which begins to appear in round dots at first isolated but soon rapidly increasing in number and size until the whole area is blackened. These investigations show that brongniardite, while possibly a distinct species under

[56] Damour, "Sur la brongniardite, nouvelle espéce minérale," *Ann. de Mines* (IV.), XVI., p. 227.

[57] Damour, "Sur la crystallization de la brongniardite, espéce minérale," *Ann. de Mines* (V.), VI., p. 146.

[58] Prior and Spencer, "Stanniferous Argyrodite from Bolivia," *Mineralogical Mag.*, Vol. 12, p. 5.

[59] Murdoch, "Microscopic Determination of the Opaque Minerals," p. 37, 1916.

the special conditions under which it was formed, has under the present conditions broken down into pyrargyrite and some other constituent or constituents not yet identified.

Schirmerite, $3(Ag_2, Pb)S, 2Bi_2S_3$.—Only one specimen of this mineral was investigated. It was from Geneva, Clear Creek Co., Colo., and represented cavity filling in quartz. It was associated with galena, chalcopyrite and covellite. The material was so scant that with the exception of covellite the relations could not be made out. Covellite appeared as borders and veinlets replacing the schirmerite.

V. THE ASSOCIATED COPPER MINERALS.

Chalcopyrite, Bornite, Chalcocite and Covellite.

Chalcopyrite.—Chalcopyrite is a very common associate of the silver minerals in many deposits while it is practically absent in others. In deposits rich in the copper minerals it plays the same rôle in replacement processes as has been found to be the case in typical copper veins. It may be either a hypogene or supergene mineral. As a hypogene mineral it is very typically found as minute dots and dashes either crystallographically arranged or scattered irregularly throughout sphalerite areas (X., *C* and XVI., *B*). The dots sometimes enlarge into more or less vein-like shapes and are thought to be due to an early replacement of sphalerite by chalcopyrite. It is further found as a hypogene mineral replacing pyrite in the form of veinlets and borders which frequently expand into areas of considerable extent. These areas, when associated with galena, are invariably found to be earlier than galena, also a hypogene mineral. Thus in Plate X., *D*, chalcopyrite is seen to have been replaced by galena.

Supergene chalcopyrite or at least chalcopyrite of a very late generation has been observed in many polished specimens of the silver ores. It occurs as borders and veinlets in galena and the late silver minerals. Thus in a specimen of argentiferous galena from Rimini, Mont., zigzag veinlets were observed following cleavage directions of galena. In Plate XVI., *D*, already described under argentite, it appears replacing that sulphide as a delicate

fringe along the borders. It is also observed replacing bornite, as described by Graton and Murdoch[60] and Tolman,[61] in the form of sharp blades often oriented in symmetrical design.

The occurrence of two generations of chalcopyrite in the silver deposits appears to be a very characteristic feature, one generation appearing just before galena, and the other later than galena or even later than the rich silver minerals.

In specimens from the Cobalt district, Ont., chalcopyrite was observed only in traces where it appeared as the late generation crossing argentite and extending into the associated smaltite (in specimen illustrated in Plate XVII., *A*).

Plate XIII., *A,* already described, illustrates a so-called intergrowth of chalcopyrite and stromeyerite from Mt. Lyell, Tasmania. Here chalcopyrite is believed to be hypogene.

Bornite.—Bornite is a comparatively rare associate of the silver minerals, being found only in the copper-silver type of deposits, as illustrated in the specimens described from Silver King, Arizona (Plate XII., *C*), and the Mt. Lyell district, Tasmania. It then generally shows the same characteristics as appear in the ordinary copper deposits, stromeyerite sometimes taking the place of chalcocite in the series of replacements. An unusual occurrence with native silver has been observed from the Cobalt district, Ont., and is illustrated in Plate XVIII., *C* and *D*.

When associated with stromeyerite and other silver minerals it has sometimes been observed to show anomalous features. In specimens from Silver King, Ariz., remnants were found showing unusual colors. On other residual grains this peculiarity appears as borders fading off almost imperceptibly into stromeyerite. It was at first thought that these effects might be due to solid solutions of stromeyerite and bornite, but on examination with high power the borders were proved to be non-homogeneous, but of such intricate structure as not to permit of photographing. The fading-off tints are due then to different relative amounts of the two minerals in a sort of sub-microscopic intergrowth, which is

[60] Graton and Murdoch, "The Sulphide Ores of Copper," *Trans. Am. Inst. Min. Eng.*, Vol. 45, p. 74, 1913.

[61] Tolman, "Observation on Certain Types of Chalcocite and their Characteristic Etch Patterns," *Trans. Am. Inst. Min. Eng.*, Vol. 52, p. 401, 1916.

simply a detail in the process of replacement. Only in the size of the particles does it differ materially from the so-called intergrowths so frequently described.

Chalcocite and Covellite.—Chalcocite is also far less common as an associate of the silver minerals than is chalcopyrite. When present it owes its origin to the same conditions which give rise to the various enrichment products of the typical copper deposits. Thus at Silver King, Arizona, it is abundant as one of the products formed from metasomatic processes in the lean pyritic ores. Here it occurs in two generations, possibly representing deposition from hypogene and supergene solutions. As a representative of the first mentioned type, it is found in rather large areas showing good cleavage in three directions when etched with potassium cyanide, and rich in the blue and white effects. The other type is shown in thin veinlets, often associated with covellite and other oxidation products crossing pyrite, chalcopyrite and bornite. Chalcocite resulting from the breakdown of stromeyerite by which native silver is also produced, has already been described (Plate XVII., *C*). As explained before the possibility of this breakdown taking place in hypogene solutions is not excluded.

Covellite, as suggested above, is often found in small quantities in silver ores, where it is believed to represent deposition from supergene solutions. It is most frequently associated with malachite in fine veinlets crossing nearly all of the earlier sulphides, but more especially sphalerite, thus recalling the first synthesis of covellite under geo-chemical conditions.[62]

VI. THE ASSOCIATED COBALT AND NICKEL MINERALS.

These minerals may all appropriately be considered in one group, since they are always intimately associated with one another and even "intergrown" in such a manner as to make separate treatment impossible.

The predominant nickel mineral is later than smaltite, as is shown in Plate XVIII., *A*, where a veinlet of niccolite crosses the

[62] Rogers, "A New Synthesis and New Occurrence of Covellite," *Sc. of Mines Quar.*, Vol. 32, p. 298, 1910–11.

cobalt mineral. The photograph also shows native silver to be still later. Relationships not so easy to interpret, however, are observed in Plate XX., *B*. Here the minerals are arranged in the spherical or concentric manner so often observed in these ores and so difficult of explanation. The outer shell consists of smaltite; this is followed by an intricate intergrowth of smaltite and niccolite, then a layer of distinct niccolite grains, while the center is occupied by native bismuth. All of these minerals are of high luster, so that etching with nitric acid was found necessary to bring out the structure for photographing. The complexity of the structure is sometimes increased by the presence of breithauptite (NiSb) intergrown with the cobalt and nickel minerals, as well as native silver, which tends to occupy the central portions and also to enter the intergrowths. Even the apparently pure smaltite areas seem to be made up of different species, as there is a slight difference of color among the various grains, and considerable variation in hardness as shown by relief. Chemical analyses have also proved that this mineral, aside from containing varying amounts of nickel (chloanthite), shows a ratio, R : As, varying from 1 : 2 to nearly 1 : 3, thus sometimes approaching skutterudite (RAs_3).[63]

The concentric structure has been explained by Campbell and Knight as due to cavity filling. Then, of course, the smaltite shell is first deposited on the interior surface of the cavity, the center being filled with the later minerals.[64] The spherical masses are grouped together in great complexity, in fact in a manner that seems to exclude the probability of their ever having been cavities. Smaltite is frequently found in calcite without the associated minerals mentioned above: then it shows a strong tendency to occur in concentric masses (Plate XX., *C*) or shell-like forms (Plate XX., *D*), the centers of which are also made up of calcite. The study of thin sections of this material shows that this is a replacement phenomenon, the unusual shapes being due to a peculiar

[63] Dana, "System of Mineralogy," 6th ed., p. 88.

[64] Campbell and Knight, "A Microscopic Examination of the Cobalt-nickel Arsenides and Silver Deposits of Temiskaming," ECON. GEOL., Vol. 1, p. 767, 1906.

habit of smaltite not yet understood. The whole calcite filling is made up of one individual and that is continuous with the calcite outside the shell as shown by identity in extinction angle, and continuance of such features as twinning bands and parting planes. This shows conclusively that smaltite has come in later than the crystallization of the calcite. The continued replacement of calcite by smaltite with the entrance of the later minerals, niccolite and bismuth, might develop a structure as appears in Plate XX., *B*, since the later arrivals, finding the spaces between the shells already occupied by smaltite, and showing a preference for calcite, would find it imperative to replace remnants of that mineral found inside the shell. Thus the early formed shells of smaltite protect the calcite centers, so that they are the last to be attacked. If this explanation is correct we should expect to find niccolite and the later minerals sometimes outside the shell for such cases as represented an incomplete earlier replacement of that calcite by smaltite. This arrangement has actually been observed in several specimens. A structure like that appearing in Plate XX., *C* would, on later replacement of calcite by niccolite, show several alternate bands of niccolite and smaltite, actual occurrences of which have also been noted. The intergrowths might easily have resulted from a replacement of smaltite by niccolite, or even by the replacement of residual calcite forming the ragged borders of some of the smaltite rings (Plate XX., *C*).

The obscure habit of smaltite to assume shell-like forms is probably connected with botryoidal structure, as shown by the fact that typical botryoidal surfaces are frequently observed on breaking specimens.

Plate XXI., *B*, shows another slight variation in the spherical structure so often assumed by smaltite. A few euhedral crystals have also developed. This specimen as well as all of the other nickel and cobalt minerals described above were from the Cobalt district, Ontario.

Many other interesting species are observed associated with the cobalt ores, but their investigation would be too remote from the purposes of this paper.

VII. THE GANGUE MINERALS.

The fact that gangue minerals must be investigated by different methods from those employed for opaque ores is perhaps responsible for the notion sometimes implied that these constitute two distinct classes of minerals. The gangue minerals form no insignificant part of vein phenomena, and their position in the sequence of deposition frequently throws light upon other important questions of paragenesis. Thus it is held by Rogers that sericite and chlorite are later than hypogene chalcocite and earlier than supergene.[65] If this conclusion is correct, as seems probable, the relation of these silicates to the ore minerals becomes of greater importance in determining paragenetic features.

The silicates when considered by themselves are found to be subject to a process of breakdown and replacement paralleled by the replacement processes of the ore minerals. Thus the feldspars break down into sericite, kaolin, carbonates and other products. The resulting minerals appear as veinlets, borders, and other forms exactly as in the case of the opaque minerals. In Plate XXI., *C*, calcite is shown replacing quartz. This is taken from the gangue of a silver specimen from Sandon, B. C. It is a photograph of a polished specimen and is a good illustration of the fact that the reflecting microscope may be a better instrument for bringing out relationships, even of the transparent minerals, than is the ordinary type. The phenomenon of replacement in Plate XXI., *C*, is not essentially different from that shown, for example, in Plate XI., *D*, which illustrates the replacement of sphalerite by tetrahedrite.

The early ore minerals are the ones most often found replacing gangue constituents, and many cases might be cited in which these processes have been described. The replacement is not confined, however, to the earlier sulphides as shown in Plate XV., *D*, where stephanite is seen to be replacing particles in a brecciated gangue. Pyrite, however, an early sulphide, is also seen to have taken part in the same kind of replacement. A similar case has already been cited from the work of Fenner in which the constituents of

[65] Rogers, "Sericite a Low-temperature Hydrothermal Mineral," Econ. Geol., Vol. 11, p. 118, 1916.

rhyolite porphyry have been replaced by chalcopyrite and stephanite. Argentiferous galena is seen to be replacing calcite along cleavage lines in Plate XXI., *D*.

Carbonates are particularly characteristic as gangue minerals of the silver ores, especially of the lead-silver type. This indicates a strong tendency for these ores to be deposited from neutral or alkaline solutions, since carbonates could not develop in acid solutions. Calcite, dolomite, siderite and rhodochrosite have frequently been noted as important associates of silver minerals. X'X, C, Siderite is shown in Plate ~~XVIII., A,~~ native silver altering to cerargyrite being seen in the same specimen.

Barite is also a frequent gangue mineral in silver deposits and has usually been described as earlier than the sulphides. Thus at Aspen, Colo., it is cut by veinlets of argentite and native silver.[66] A similar occurrence was observed in material from Sandon, B. C., in which thin sections showed argentite replacing barite in fringes along the borders of euhedral crystals.

VIII. THE IDENTIFICATION OF SILVER MINERALS ON POLISHED SURFACES.

A good summary of the work thus far accomplished on methods for the determination of the opaque minerals has already been given by Murdoch.[67] From this it will appear that very little detailed study had been made of the silver minerals. In Murdoch's tables they are grouped according to color, hardness, and action of various reagents as KCN, HNO_3, etc. Argentite, polybasite and stephanite are put down as grayish white; silver, dyscrasite and huntilite as creamy white and proustite and pyrargyrite as bluish white. His etching and tarnishing tests are not characteristic and have been found of little value for purposes of identification.

As stated in the introduction three important means have been employed for the identification of the silver minerals discussed

[66] Spurr, "Geology of the Aspen Mining District," Mon. U. S. Geol. Surv., Vol. 31, p. 221, 1898.

[67] Murdoch, "Microscopic Determination of the Opaque Minerals," pp. 4–16, 1916.

in this paper. First, the observation of color, relief and habit as observed on polished surfaces; second, the study of minute fragments broken from the surface by a sharp point and transferred to a glass slip for examination with an ordinary microscope; and third, by micro-chemical tests on small fragments secured in the same manner. Etching with nitric acid has been found valuable in the study of argentiferous galena (Plate XI., *A* and C), the silver minerals being less easily attacked by this reagent than galena; for bringing out structure for purposes of photographing as in huntilite (Plate XIX., *D*); and for developing structure in the bismuth-cobalt specimens (Plate XX., *B*). Potassium cyanide has been found especially useful in bringing out the complicated structure of stromeyerite and in distinguishing it from chalcocite (Plate XIII., *B* and *C*).

Hardness and color are best compared with galena, since that mineral is the one most commonly associated with the silver minerals. In this respect the tables of Murdoch have been found of great value. All of the silver minerals with the exception of tetrahedrite are softer than galena and therefore stand in negative relief. Even tetrahedrite as it becomes highly argentiferous approaches galena in hardness. The normal varieties are considerably harder. Proustite is probably the one that can be most easily distinguished by color alone. It has a characteristic bluish tint rarely mistaken for that of other minerals. Pyrargyrite, in the writer's opinion, is not perceptibly blue in color, being practically of the same tint as some tetrahedrite and polybasite. It can, however, readily be distinguished from tetrahedrite by its inferior hardness, and from each by chemical tests described below.

Tests on fragments are made by breaking from the polished surface minute quantities of the mineral by means of a sharp awl, transferring to a glass slip and examining with a high power microscope. Argentite and stephanite are opaque even on the thinnest edges. Proustite is transparent even in the thicker portions, and is of a beautiful red color, shading off into amber on the thinnest edges. Pyrargyrite is transparent and of a deep cherry red color only on thin edges, the thicker portions even ap-

proaching opacity. Polybasite and some specimens of tetrahedrite react in the same way as pyrargyrite but the presence of copper in these minerals is a distinguishing feaure. In making these tests as bright a light as possible should be used and care should be exercised in focusing carefully, otherwise interference of light on sharp edges of black fragments may produce red tints. Proustite and pyrargyrite may also be distinguished by their streak, a test which can also be made on very small fragments by crushing on white paper. In securing the material by means of a sharp point, the sectility of argentite is a sufficient test for distinguishing that mineral.

Micro-chemical tests are made by securing a minute portion of the powder in the manner described above, transferring to a glass slip, dissolving in nitric acid by warming slightly, evaporating nearly to dryness, taking up in a drop of distilled water and proceeding as outlined below.

The presence of silver is learned by adding a drop of dilute chlorhydric acid. The characteristic curdy precipitate is satisfactory evidence. Comparative tests may be made on known minerals so as to be able to judge if the silver be present in large or small amounts.

Copper is tested for by adding potassium ferrocyanide in a slightly acid solution. The peculiar red precipitate is thoroughly characteristic of this element and may even be seen in the presence of iron if the drop of reagent is allowed to stand without mixing. Some phenomenon of diffusion permits the two precipitates to be seen.

The two tests outlined above are the ones most often required in distinguishing the silver minerals and it has been found much more satisfactory to remove the minute amount of material required, than to attempt making the test directly on the surface. Moreover by this method the specimen is much less damaged for further work. Having obtained the material in solution as outlined above, tests may be made for other elements according to the methods outlined by Chamot for general micro-chemical work.[68] In the investigation of the cobalt-nickel minerals the

[68] Chamot, "Elementary Chemical Microscopy," 1915.

dimethylglyoxime test for nickel has been found to be especially useful. This is made by making the solution alkaline, placing a minute crystal of the oxime in the solution, covering with a cover-glass and examining after allowing to stand for some time. By using the solid reagent the red needles of the nickel salt collect around the crystal and the test is believed to be more delicate. The test is satisfactory in the presence of large amounts of iron, the needles easily being seen mingled with the hydroxid. Thus a specimen of socalled nickeliferous pyrrhotite, said to contain not more than three per cent. nickel, responded satisfactorily to the test.

In the table below only tests are listed that have been found to be particularly useful in distinguishing the common silver minerals. Those most typical are marked with a star.

	Color.	Fragments.	Hardness.	Chem. Tests.	Others.
Argentite	Grayish.	Opaque.	Less than galena.	Ag.	Sectile.*
Polybasite ...	"	Red on edges.*	Less than galena.	Ag* and Cu.*	——
Pyrargyrite ..	"	" " " *	Less than galena.	Ag.	Purple red streak.
Stephanite...	"	Opaque.*	Less than galena.	Ag.	——
Tetrahedrite .	"	Sometimes red on edges.	Greater than galena.*	Cu* and (Ag.)	——
Proustite	Bluish.*	Red.*	Less than Gn.	Ag.	Red streak.
Stromeyerite .	Purplish with chalcocite.*	Opaque.	= Gn.	Cu and Ag.*	——

Stephanite and argentite are both opaque, but argentite may be distinguished by its sectility.

Pyrargyrite and polybasite are each red on thin edges, but polybasite reacts for copper.

Polybasite and tetrahedrite may each be red on thin edges, each react for copper, but tetrahedrite is easily distinguished by its greater hardness.

A delicate test for arsenic and antimony so as to distinguish between tennantite and tetrahedrite, as well as between polybasite and pearceite, is greatly needed. Berg recommends for the sulfo-salt minerals the following test: Dissolve a fragment

in potassium hydroxid solution, then add chlorhydric acid. Arsenic if present is thrown down as the lemon yellow sulphide. The corresponding antimony minerals give an orange precipitate.[69] While this works well for pure compounds, it has been found to be of little value in studying the complex mixture observed in this class of minerals.

IX. RESUMÉ.

1. Tetrahedrite and argentiferous galena are the early sources of the rich silver minerals. Much of this galena has replaced tetrahedrite, so the latter mineral becomes the more important of the two.

2. The minerals antedating the deposition of silver in the ore body are, in the order of sequence, arsenopyrite, pyrite and sphalerite.

3. Graphic structures are frequently observed among the silver minerals and their associates. Those described are of two classes: First, those of undoubted replacement, and second, those of unproved origin but thought to be due to simultaneous deposition with later crystallization and segregation after graphic designs. To the first class belong the following so-called intergrowths: Stromeyerite and chalcopyrite (Plate XIII., *A*); bornite and stromeyerite (Plate XII., *D*); and bornite and native silver (Plate XVIII., *D*). To the second class belong the more intricate intergrowths between the following minerals: Stromeyerite and chalcocite (Plate XIII., *B* and *C*); stromeyerite and galena (Plate XIV., *A*); stromeyerite and argentite; galena and proustite (Plate XV., *B*); and pyrargyrite and some mineral not yet identified (in socalled brongniardite (Plate XX., *A*)).

4. Galena which does not show abundant evidence of later additions or enrichments has not been observed to contain more than 0.35 per cent. silver, the average of fifteen specimens from rich silver-lead deposits being 0.20 per cent. This may be present in solid solution or sub-microscopic particles up to nearly 0.10 per cent. Above that amount it appears as spots of definite minerals

[69] Berg, "Mikroskopische Untersuchung der Erzlagerstätten," p. 46.

identified as tetrahedrite or argentite or both. Specimens of galena with more than about 0.35 per cent. silver show evidence of later addition of ruby silver or other rich silver minerals in the form of veinlets.

5. Whether the "enrichment" of the silver ores is due to ascending or descending solutions has not been decided. Probably both factors are active. The writer is inclined to attribute greater activity in this respect to hypogene solutions than is general among economic mineralogists. This is due mainly to the fact that microscopic examination of mineral deposits shows a continuous series of replacements to have occurred and often there is no reason for considering those concerned with the deposition of the late silver minerals as different in kind from the earlier processes.

6. Certain of the silver minerals, notably argentite and pyrargyrite, are rapidly blackened on polished surfaces by an unprotected electric arc, a feature that has been found of use in identification.

7. The complicated structure of stromeyerite seen in some specimens is the result of a mixture of stromeyerite and chalcocite. Stromeyerite is believed to be a definite double salt of silver sulphide and copper sulphide. Chalcocite probably is able to hold some silver sulphide in solid solution but the limit of solubility has not been worked out.

8. The peculiar concentric structure seen in cobalt-nickel minerals is believed to be due to the habit of the early mineral, smaltite, to replace calcite in the form of concentric shells. The later minerals replacing the remainder of the calcite inside the shells complete the structure. The spaces between the shells are sometimes filled (by replacement of calcite) with the early mineral smaltite, less often by the later mineral niccolite.

9. Micro-chemical tests applied on fragments secured from the polished surfaces are considered more useful in identifying silver minerals than the etching or tarnishing methods.

10. The order of deposition of the minerals in silver deposits is outlined below. Important deviation from this order has not been observed.

I. Silver-lead-zinc series.

(1) Pyrite, (2) sphalerite, (3) tetrahedrite, (4) galena, (5) ruby silver, polybasite, stephanite, etc., (6) native silver. Chalcopyrite in this series appears quite typically in two generations, one replacing any one or all of the sulphides earlier than galena, the other later than galena and the rich silver minerals.

II. Copper-silver series.

(1) Pyrite, (2) chalcopyrite, (3) bornite, (4) chalcocite, stromeyerite and argentite, (5) silver. Galena when present is probably between chalcopyrite and bornite.

III. Cobalt-silver series.

(1) Smaltite (chloanthite), (2) niccolite (briethauptite), (3) argentite, (4) silver and bismuth.

X. ACKNOWLEDGMENTS.

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The investigations were conducted in the laboratories of the Department of Geology of Leland Stanford Junior University, and the author wishes to acknowledge his indebtedness to Professor C. F. Tolman, Jr., and Professor A. F. Rogers, whose helpful suggestions and useful criticisms are greatly appreciated.
helpful advice and useful criticisms are greatly appreciated.

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EXPLANATION OF PLATE X.

FIG. A. ($\times$ 21.) Pyrite (*py*) crossed and bordered by chalcopyrite (*cp*) with later sphalerite (*sl*), galena (*gn*) and stephanite (*st*). Sandon, B. C.

FIG. B. ($\times$ 61.) Arsenopyrite (*as*) and pyrite (*py*) replaced by galena (*gn*). Proustite (*ps*) in galena areas.

FIG. C. ($\times$ 61.) Sphalerite (*sl*), argentiferous tetrahedrite (*td*) and galena (*gn*). Sphalerite dotted with chalcopyrite. Silver King mine, near Globe, Arizona.

FIG. D. ($\times$ 21.) Argentiferous tetrahedrite (*td*) and chalcopyrite (*cp*) replaced by galena (*gn*). Sphalerite (*sl*). Silver King, Arizona.

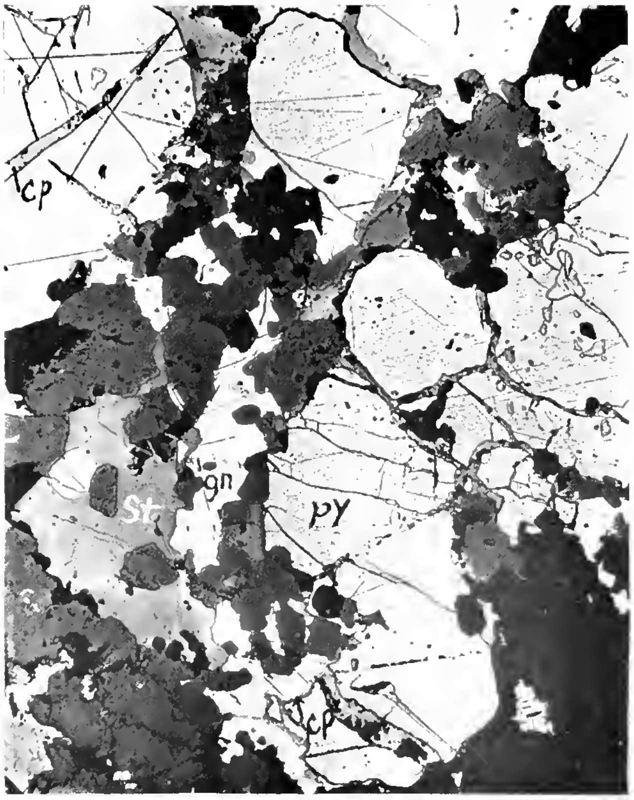

FIG. A.

FIG. B.

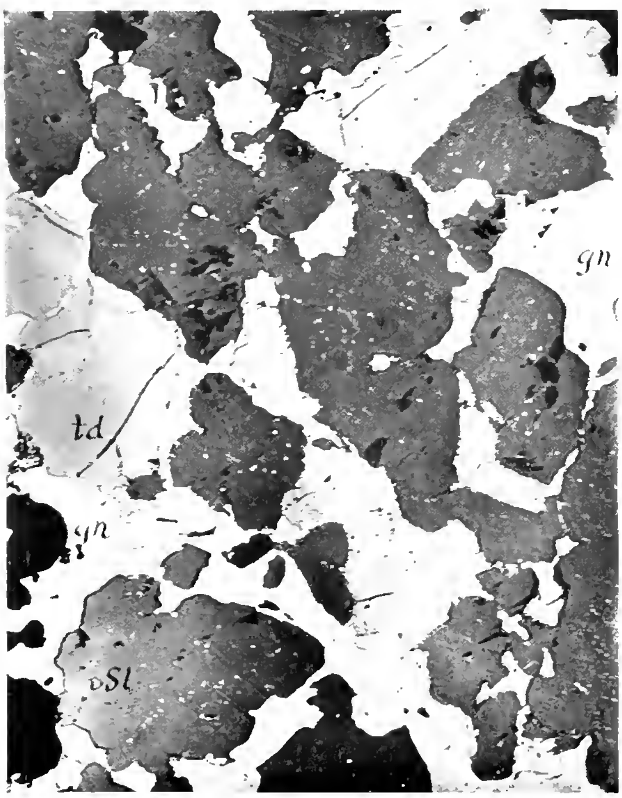

FIG. C.

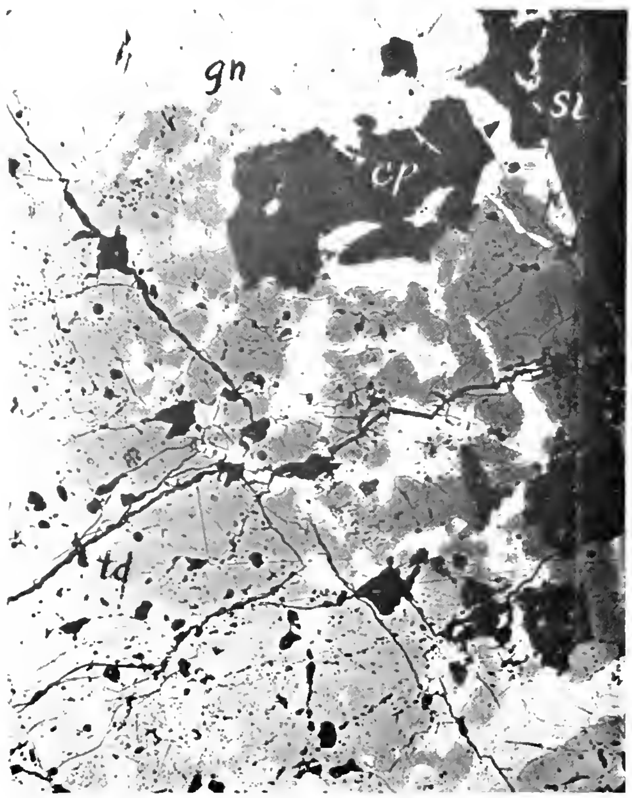

FIG. D.

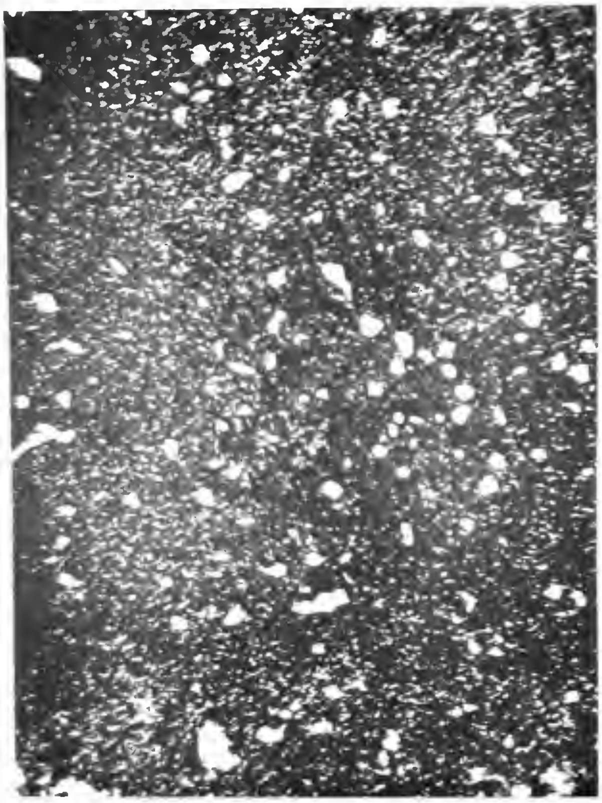

FIG. A.

FIG. B.

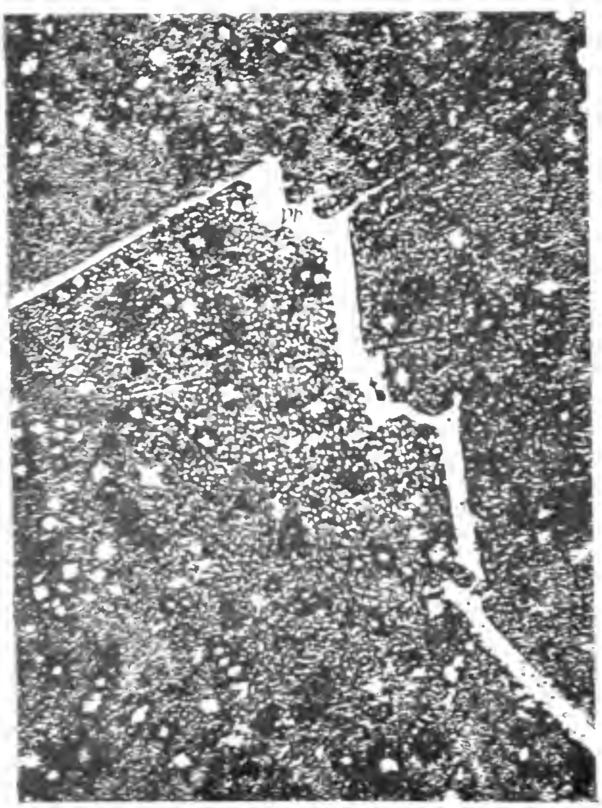

FIG. C.

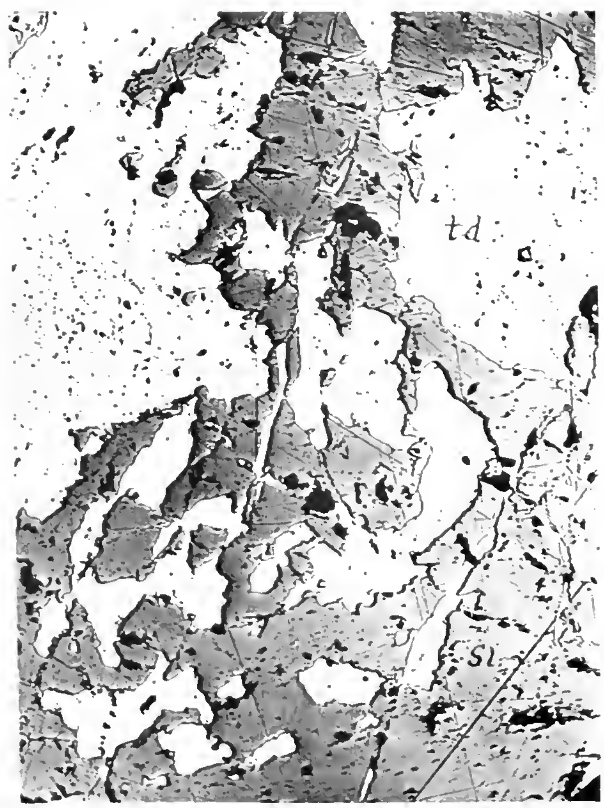

FIG. D.

EXPLANATION OF PLATE XI.

FIG. A. (× 201.) Galena containing .35 per cent. silver showing spots of tetrahedrite and other silver minerals. Etched with nitric acid. Rimini, Montana.

FIG. B. (× 336.) Galena (*gn*) showing spots of proustite (*ps*). Tonopah, Nevada.

FIG. C. (× 257.) Pyrargyrite following cleavage directions in galena. Etched with nitric acid. Sandon, B. C.

FIG. D. (× 301.) Sphalerite (*sl*) replaced by tetrahedrite (*td*). Silversmith mine, Sandon, B. C.

EXPLANATION OF PLATE XII.

FIG. A. ($\times$ 57.) Stromeyerite (*so*) replacing tetrahedrite (*td*) in a complex system of veinlets. Silver King, Arizona.

FIG. B. ($\times$ 170.) Stromeyerite (*so*) replacing tetrahedrite (*td*) in cracks and along the borders of quartz gangue. Colorado.

FIG. C. ($\times$ 223.) Replacement of chalcopyrite (*cp*) by bornite (*bn*) with veinlet of stromeyerite (*so*) crossing each. Native silver (*s*) is the last mineral to form. Large area of stromeyerite shows complex surface due to excess of the chalcocite molecule. Silver King, Arizona.

FIG. D. ($\times$ 61.) Replacement of bornite (*bn*) by stromeyerite (*so*) in coarse craphic design. Silver King, Arizona.

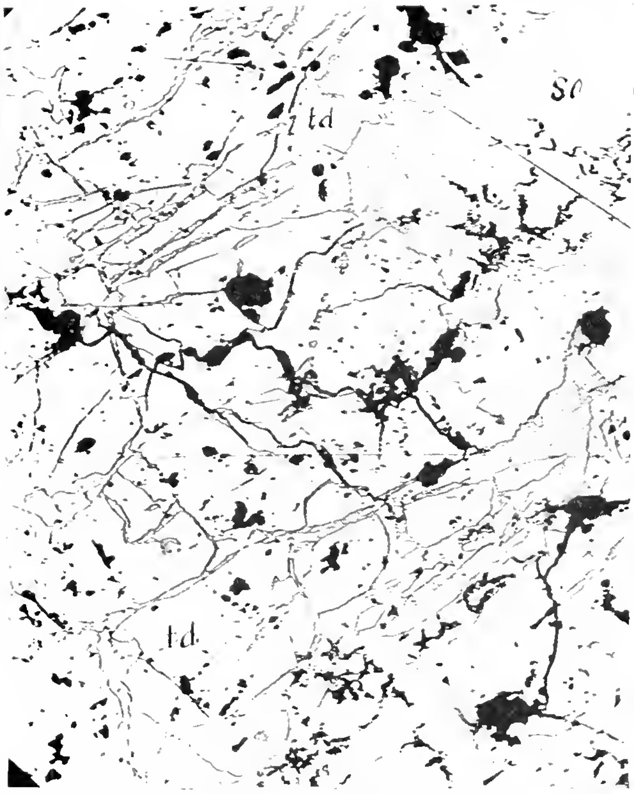

FIG. A.

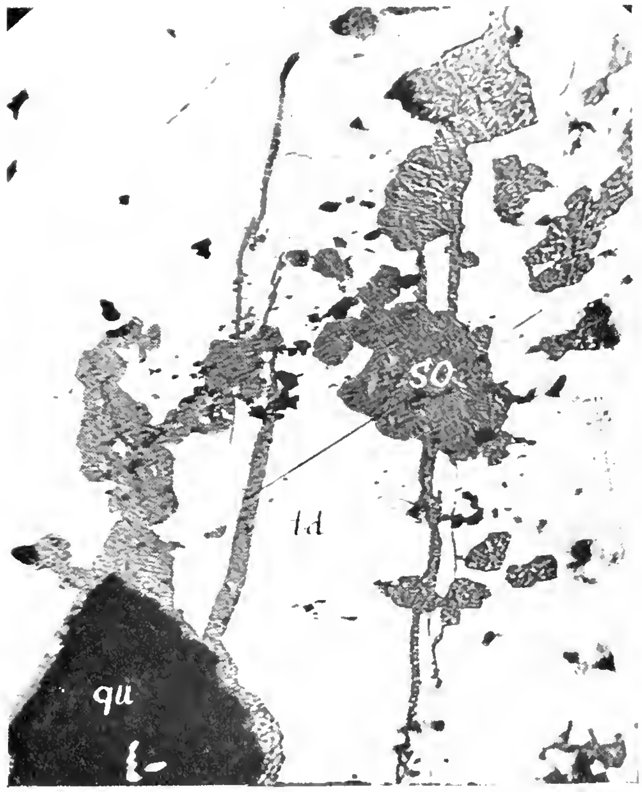

FIG. B.

FIG. C.

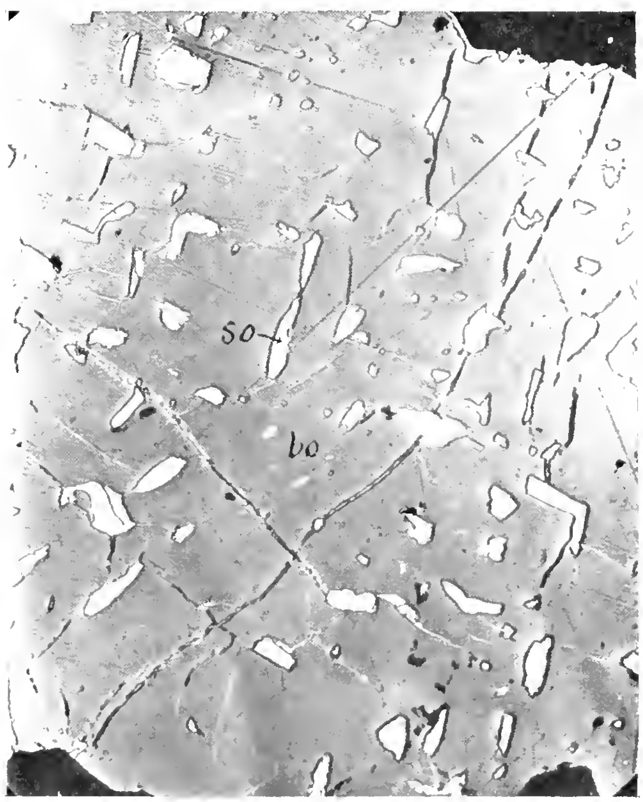

FIG. D.

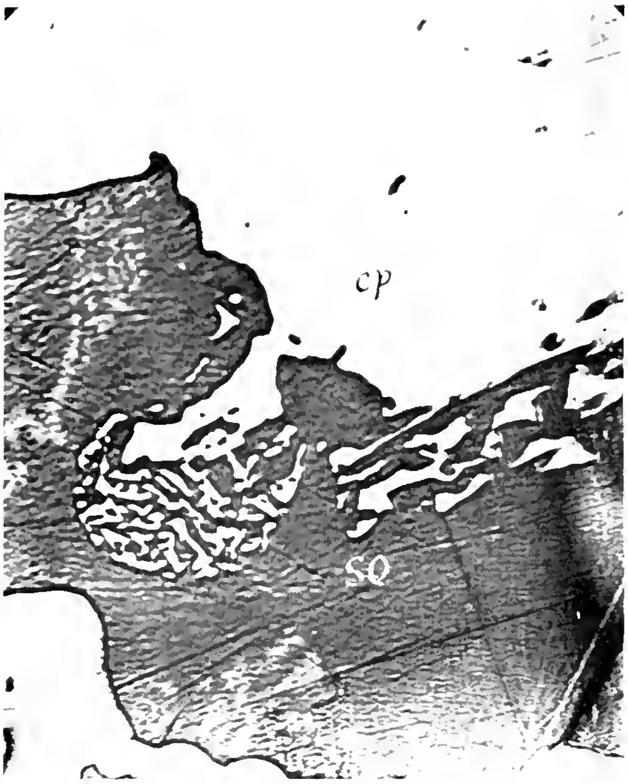

FIG. A.

FIG. B.

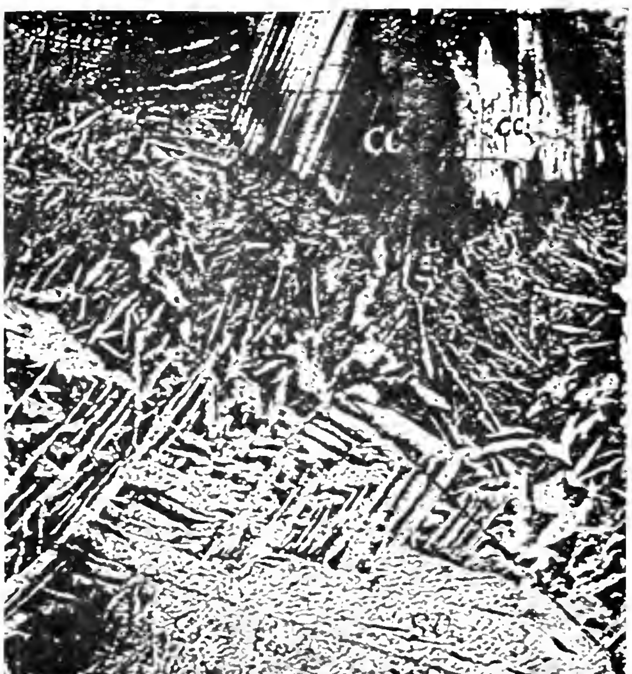

FIG. C.

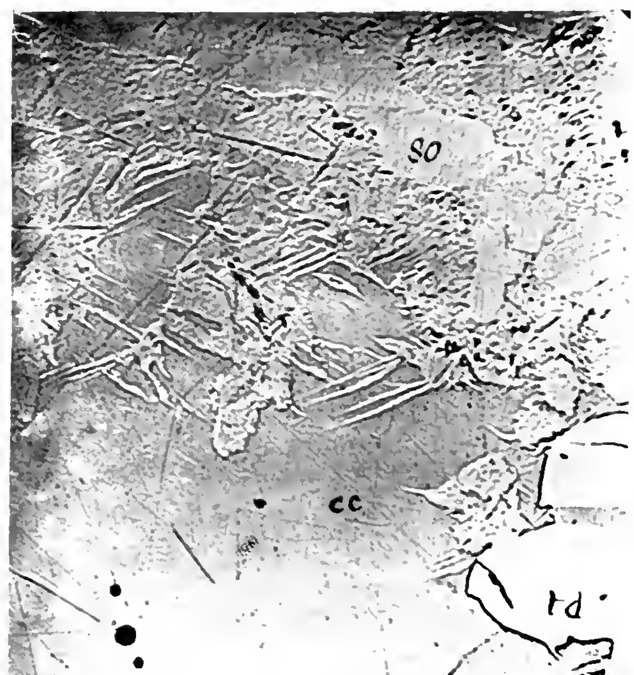

FIG. D.

EXPLANATION OF PLATE XIII.

FIG. A. (× 267.) Replacement of chalcopyrite (*cp*) by stromeyerite (*so*), leaving residual grains grouped in graphic design. Mt. Lyell, Tasmania.

FIG. B. (× 98.) Stromeyerite etched with potassium cyanide solution to bring out structure. Leaf-shaped masses are pure stromeyerite. The black portion more strongly attacked is chalcocite. Silver King, Arizona.

FIG. C. (× 288.) Pure stromeyerite areas (*so*) grading into chalcocite (*cc*). The border between the two shows structure of Fig. B, due to mixture of the two. Unknown locality, Arizona.

FIG. D. (× 288.) Same as Fig. C but not etched. Residual mass of tetrahedrite also shown (*td*). Arizona.

EXPLANATION OF PLATE XIV.

Fig. A. (× 603.) So-called intergrowth of galena (light) and stromeyerite (dark). Silver King, Arizona.

Fig. B. (× 262.) Sphalerite (*sl*) crossed by a veinlet of galena (*gn*) and proustite (*ps*). Schemnitz, Hungary.

Fig. C. (× 77.) Proustite filling cavities between euhedral quartz crystals (*q*) and altering to native silver (*s*). Durango, Mexico.

Fig. D. (× 81.) Pyrargyrite (*pr*) and proustite (*ps*) filling cavities in quartz gangue (*q*). Pyrargyrite slightly tarnished by electric light, thus showing contrast otherwise almost imperceptible. Tonopah, Nevada.

FIG A.

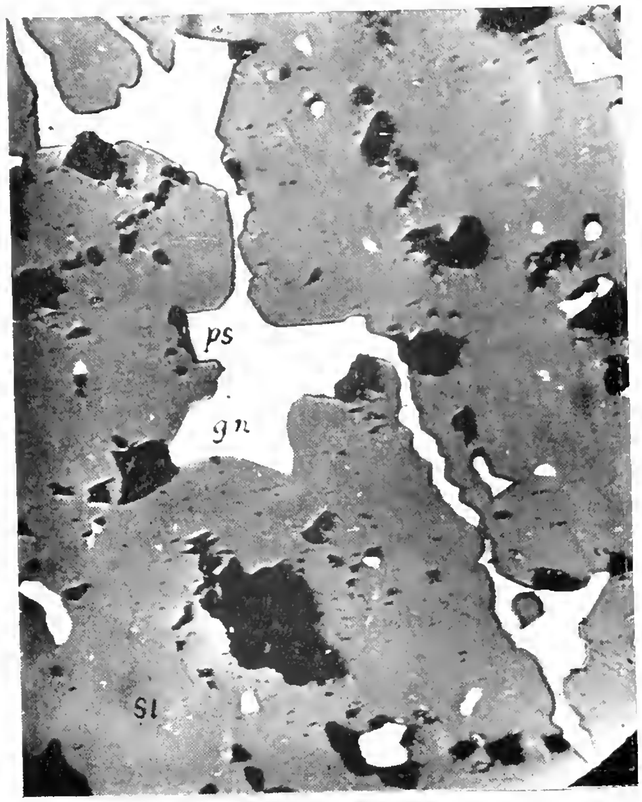

FIG. B.

FIG. C.

FIG. D.

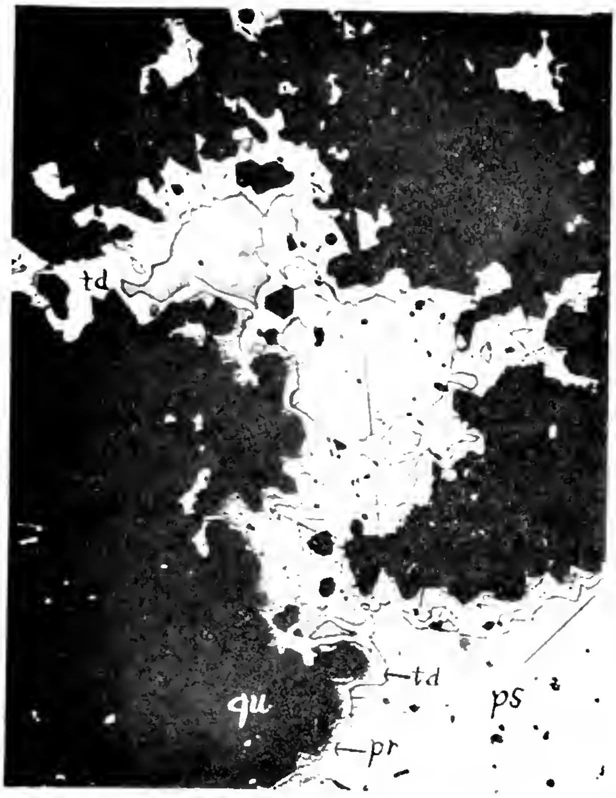

FIG. A.

FIG. B.

FIG. C.

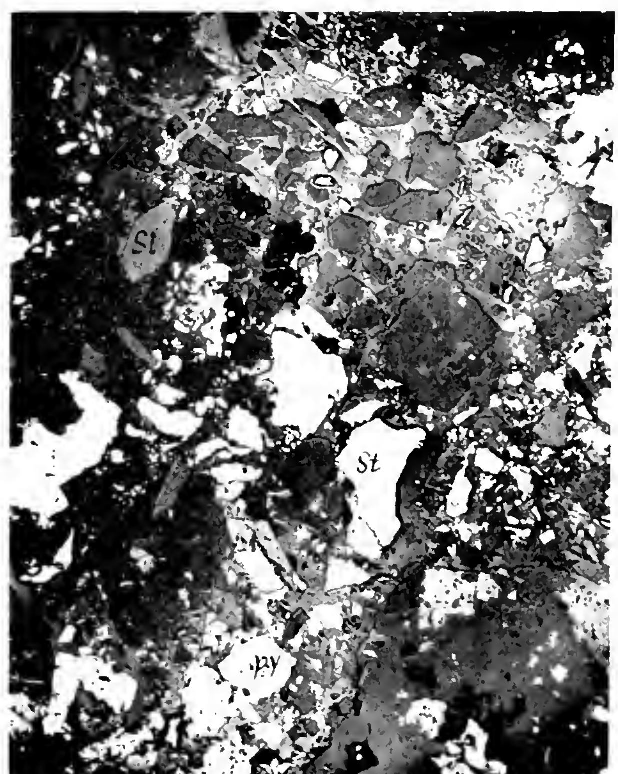

FIG. D.

EXPLANATION OF PLATE XV.

FIG. A. (× 74.) Pyrargyrite (*pr*), proustite (*ps*) and tetrahedrite (*td*) in cavities in quartz gangue. This is part filling and part replacement. Tonopah, Nevada.

FIG. B. (× 881.) An area of so-called intergrowth of proustite (*ps*) and galena (*gn*) occurring as a residual mass in pyrargyrite (*pr*). Pyrargyrite was blackened by action of electric light employed in photographing. Schemnitz, Hungary.

FIG. C. (× 47.) A late generation of iron disulfid (marcasite, *ma*) in a background of proustite and pyrargyrite in intimate mixture. Cobalt, Ontario.

FIG. D. (× 19.) The sulfids, pyrite (*py*), sphalerite (*sl*) and stephanite (*st*) replacing fragments in a brecciated gangue consisting mostly of quartz. Sandon, B. C.

EXPLANATION OF PLATE XVI.

FIG. A. ($\times$ 94.) Sphalerite (*sl*), galena (*gn*) and stephanite (*st*). Schemnitz, Hungary.

FIG. B. ($\times$ 48.) Sphalerite (*sl*) with dots of chalcopyrite (*cp*) replaced by veinlet of galena (*gn*). Small patches of polybasite (*pb*) later replaces galena. Guanacevi, Mexico.

FIG. C. ($\times$ 41.) Argentite (*ar*) replaced by a late generation of iron disulfid, pyrite or marcasite (*py*). Freiberg, Saxony.

FIG. D. ($\times$ 265.) Argentite (*ar*) replaced around borders by a fringe of late generation chalcopyrite (*cp*). Argentite is blackened by the electric light. Butte, Montana.

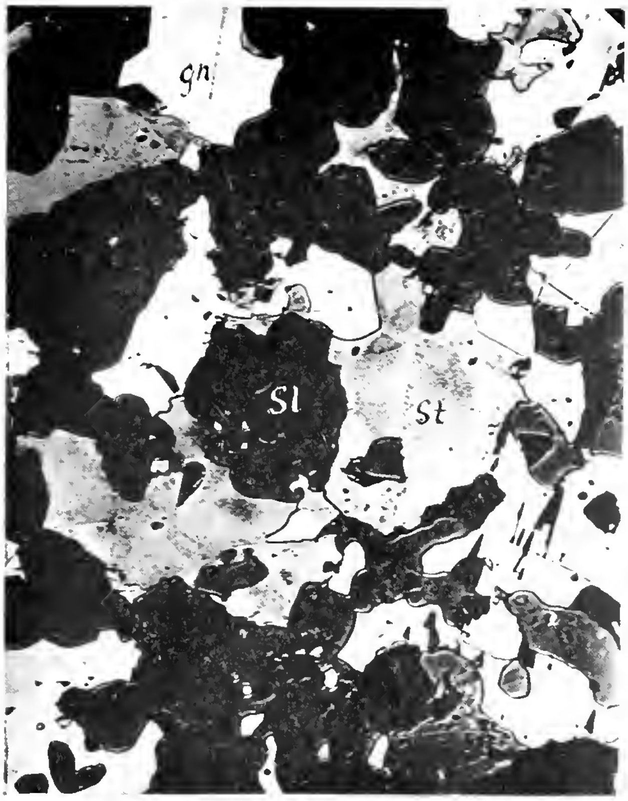

Fig. A.

Fig. B.

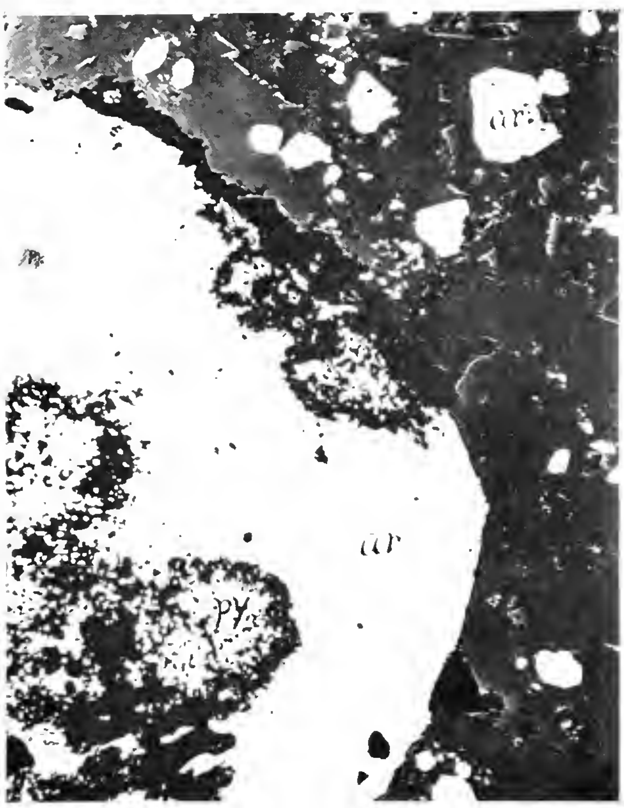

Fig. C.

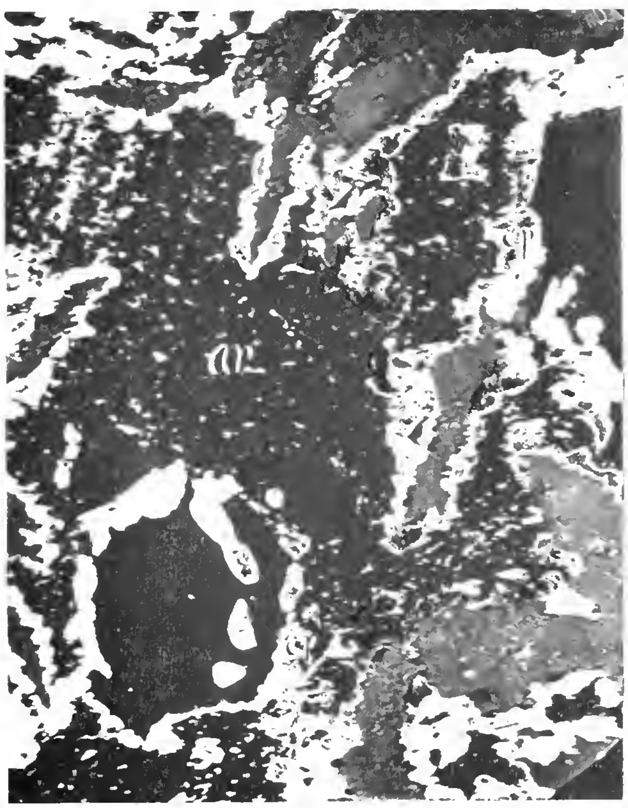

Fig. D.

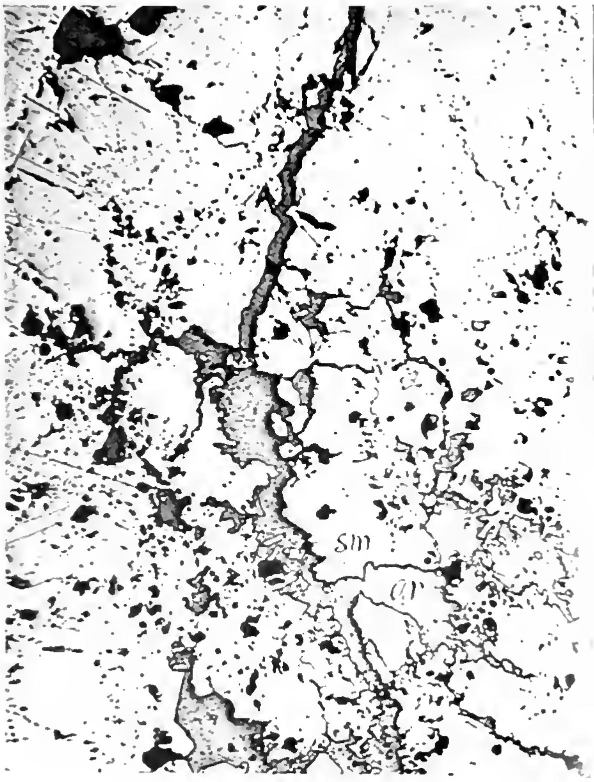

FIG. A.

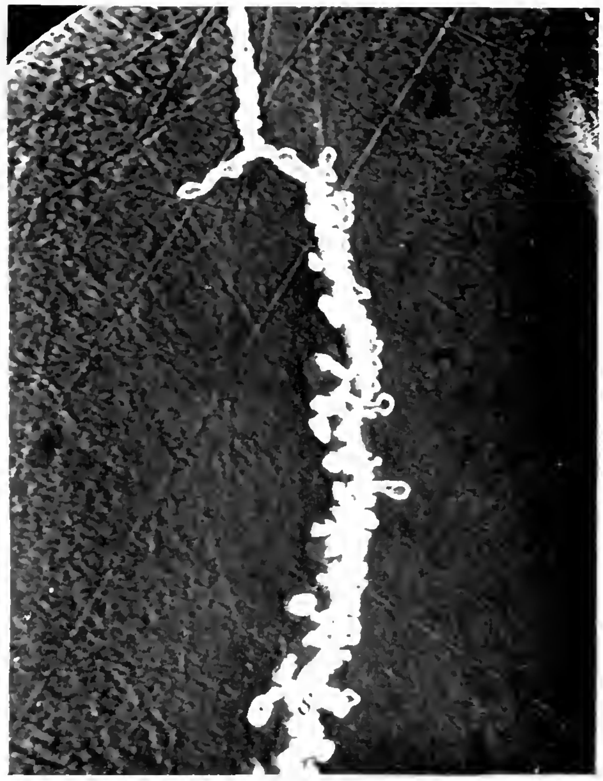

FIG. B.

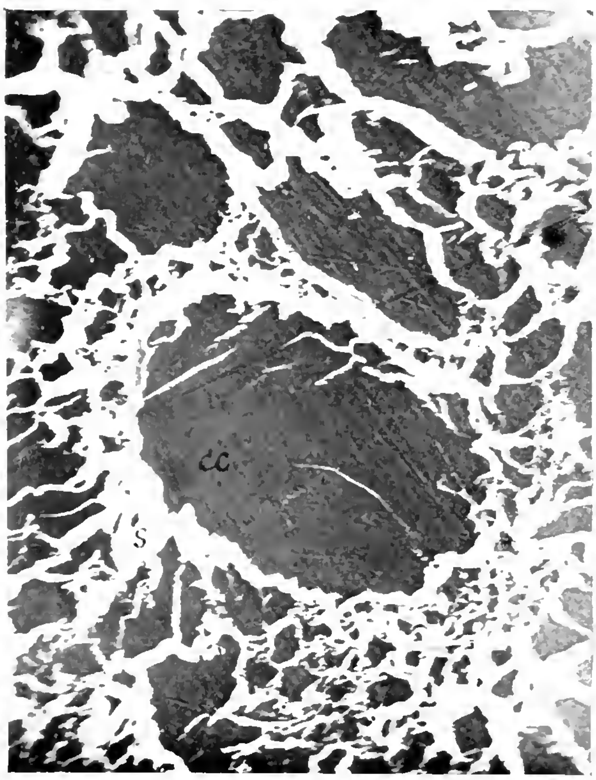

FIG. C.

FIG. D.

EXPLANATION OF PLATE XVII.

FIG. A. (× 48.) Veinlet of argentite (*ar*) in smaltite (*sm*). Cobalt, Ontario.

FIG. B. (× 94.) Veinlet of native silver (*s*) in argentite (*ar*). Butte, Montana.

FIG. C. (× 223.) Native silver (*s*) in chalcocite (*cc*). This structure frequently results from the breakdown of stromeyerite. Silver King, Arizona.

FIG. D. (× 9.) Native silver (*s*) in veinlet of tetrahedrite (*td*) which crosses smaltite (*sm*). Cobalt, Ontario.

EXPLANATION OF PLATE XVIII.

FIG. A. (× 102.) Veinlet of niccolite (*nc*) in smaltite (*sm*), followed up by native silver (*s*). Cobalt, Ontario.

FIG. B. (× 48.) Native silver (*s*) replacing smaltite (*sm*). Euhedral crystals of smaltite embedded in silver form a characteristic feature of these ores. Cobalt, Ontario.

FIG. C. (× 224.) The replacement of bornite (*bn*) by native silver (*s*). Cobalt, Ontario.

FIG. D. (× 380.) Replacement of bornite (dark) by native silver (light) approaching the so-called graphic intergrowth. Cobalt, Ontario.

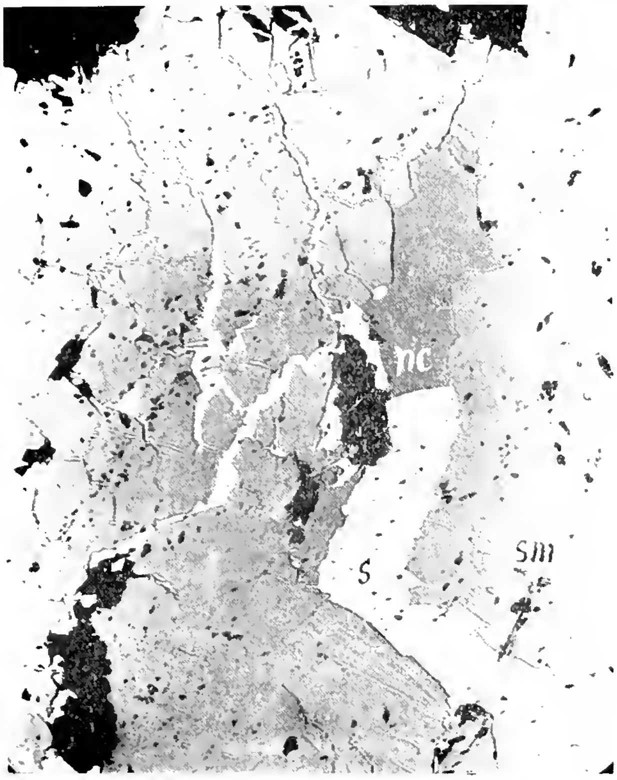

FIG. A.

FIG. B.

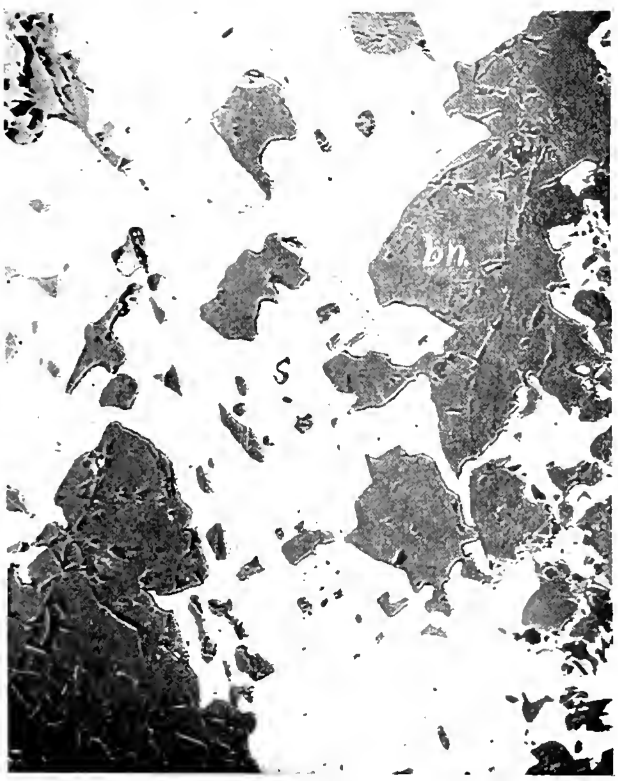

FIG. C.

FIG. D.

FIG. A.

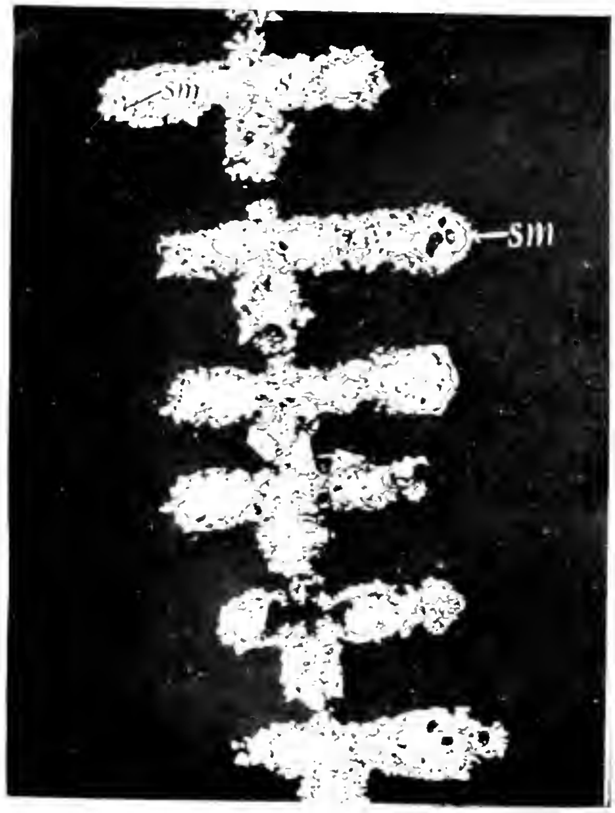

FIG. B.

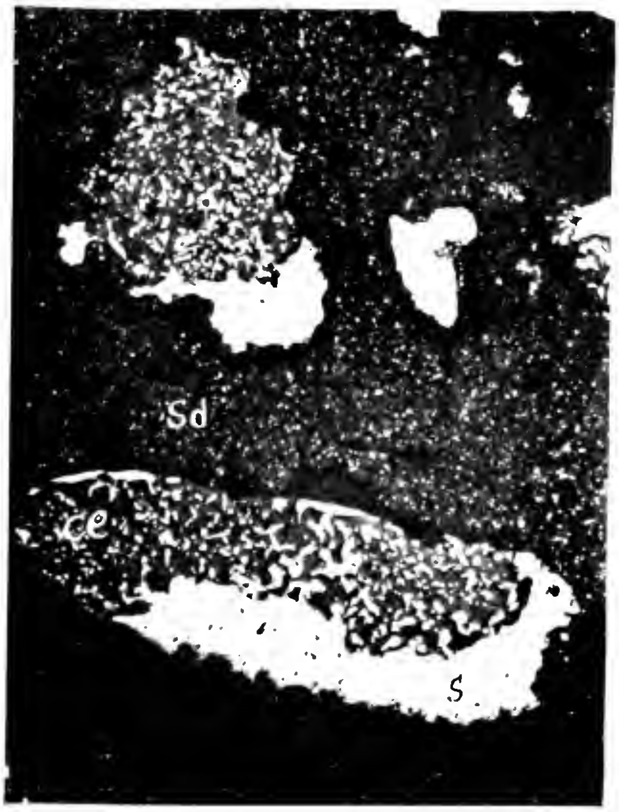

FIG. C.

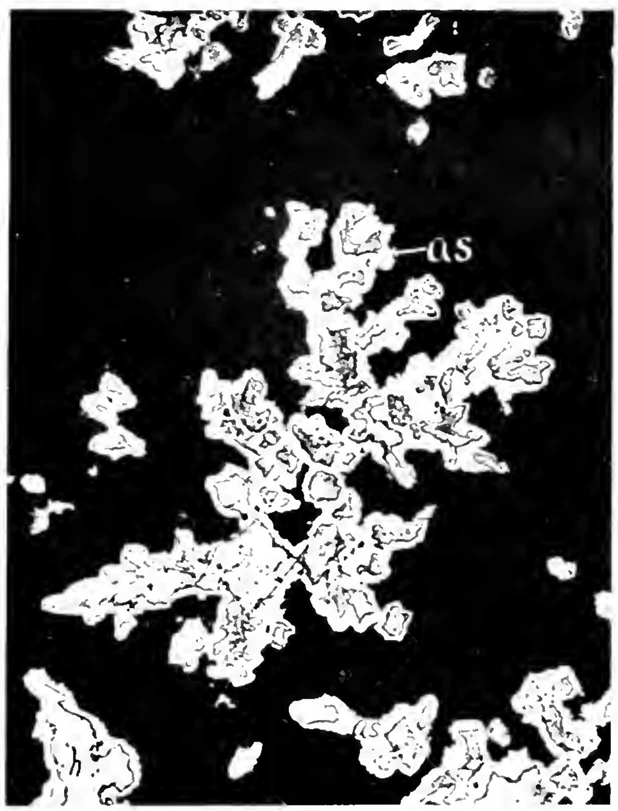

FIG. D.

EXPLANATION OF PLATE XIX.

FIG. A. ($\times$ 9.) Dendritic silver and smaltite in calcite. Cobalt, Ontario.

FIG. B. ($\times$ 48.) The same as Fig. A under higher magnification. A central portion of native silver (*s*) is seen with a thin shell of smaltite (*sm*). Cobalt, Ontario.

FIG. C. ($\times$ 21.) Native silver (*s*) in siderite (*sd*) altered to cerargyrite (*ce*). Stonewall Jackson mine, near Prescott, Arizona.

FIG. D. ($\times$ 56.) So-called huntilite (*hu*) with rim of native arsenic (*as*) in a carbonate gangue. Silver Islet, Lake Superior.

EXPLANATION OF PLATE XX.

FIG. A. (× 223.) Micro-structure of so-called brongniardite, showing a breakdown into pyrargyrite (dark lines) and unknown constituents. Pyrargyrite lines show etching by electric light. Chococomete, Bolivia.

FIG. B. (× 74.) Native bismuth (*bi*) with silver occupying the center of a series of concentric shells made up of niccolite (*nc*) followed by an intergrowth of niccolite, breithauptite, smaltite and chloanthite (*nc* and *sm*) and then smaltite-chloanthite (*sm*). Cobalt, Ontario.

FIG. C. (× 9.) Concentric shells of smaltite (chloanthite) in calcite gangue. Cobalt, Ontario.

FIG. D. (× 11.) Shells of smaltite replacing calcite gangue. Cobalt, Ontario.

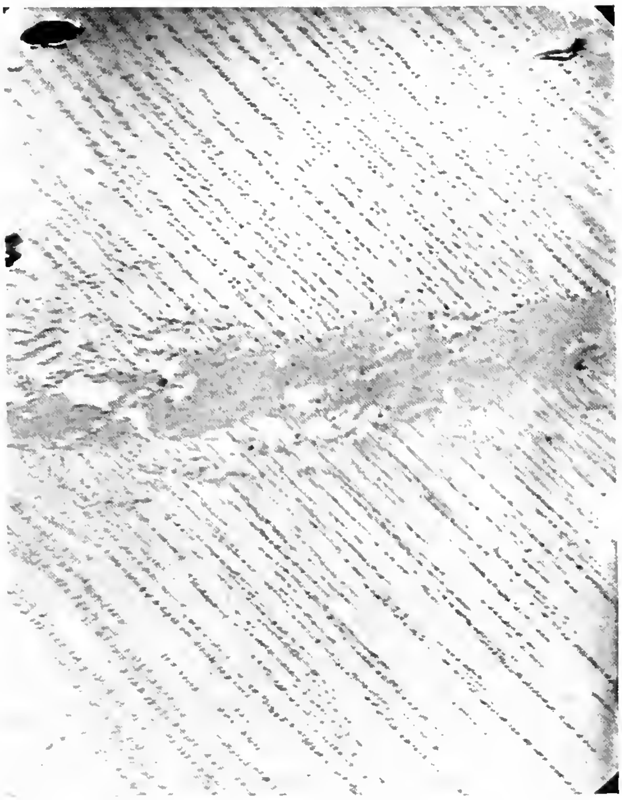

FIG. A.

FIG. B.

FIG. C.

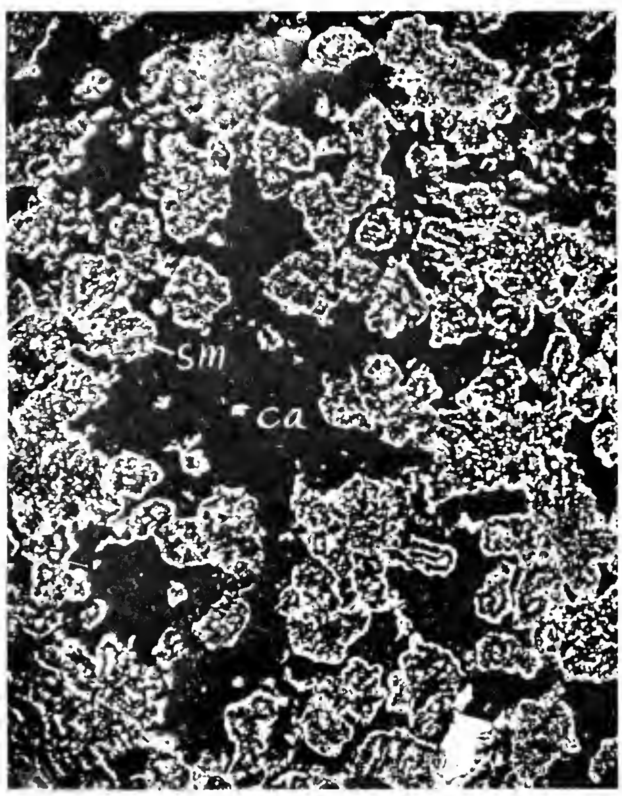

FIG. D.

FIG. ~~1~~. D

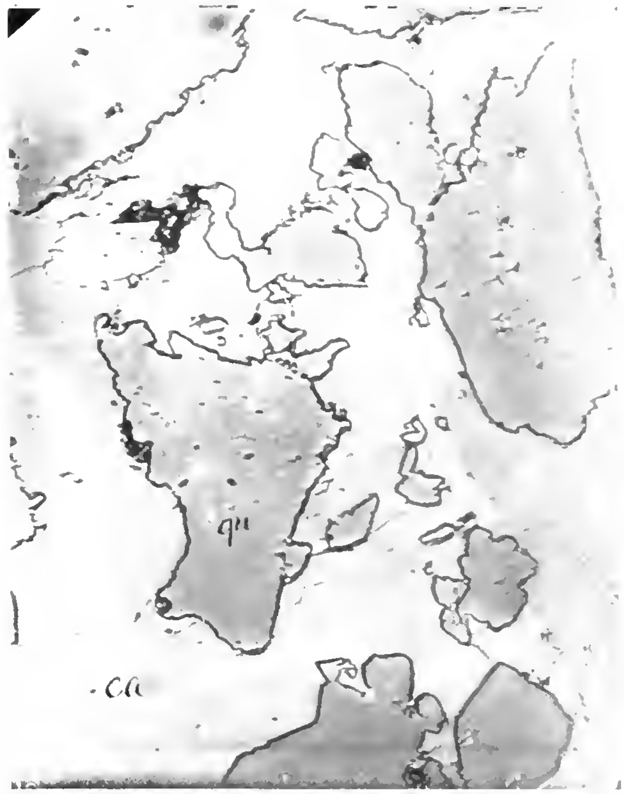

FIG. ~~1~~. C,

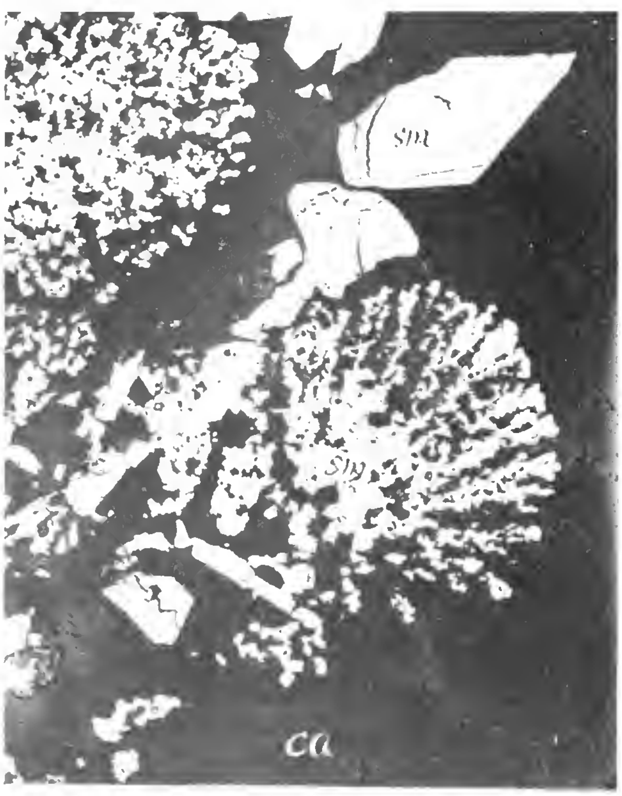

FIG. ~~1~~. B,

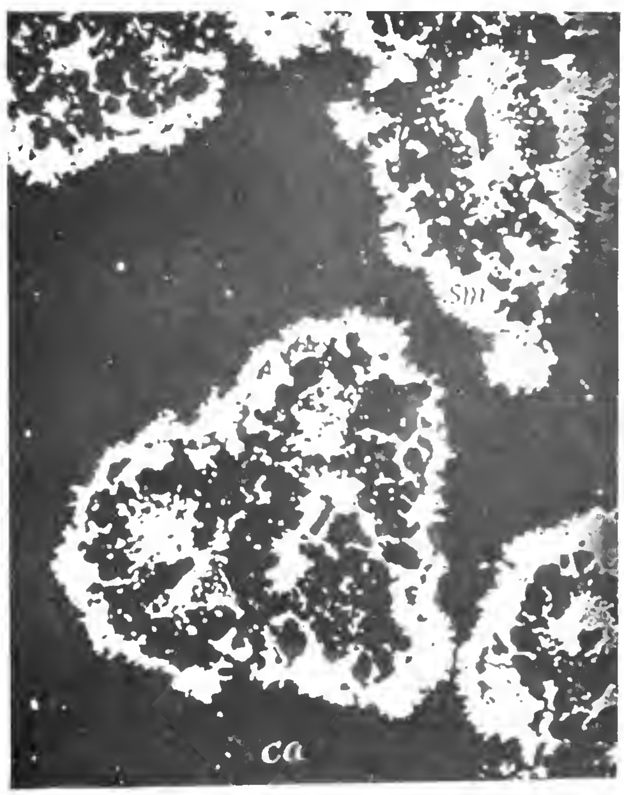

FIG. ~~1~~. a,

EXPLANATION OF PLATE XXI.

Fig. A. (× 53.) Same as Fig. C (Plate XX.), showing individual shells under higher power. Cobalt, Ontario.

Fig. B. (× 48.) Smaltite (*sm*) replacing calcite (*ca*) in peculiar radiating forms. Cobalt, Ontario.

Fig. C. (× 288.) Gangue minerals. Calcite (*ca*) replacing quartz (*qu*). Sandon, B. C.

Fig. D. (× 74.) Galena (*gn*) replacing calcite gangue (*ca*) along cleavage directions. Broken Hill, Australia.